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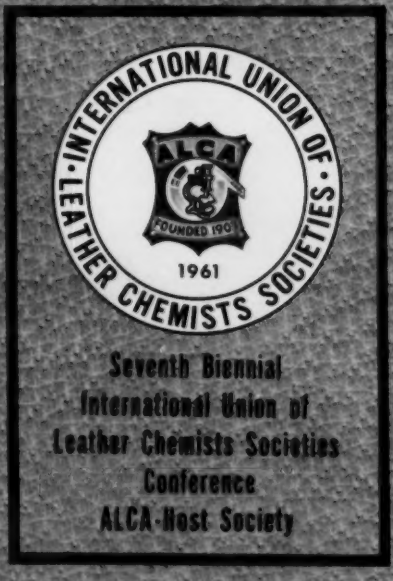

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The Journal

of the

AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LVI AUGUST 1961 No. 8

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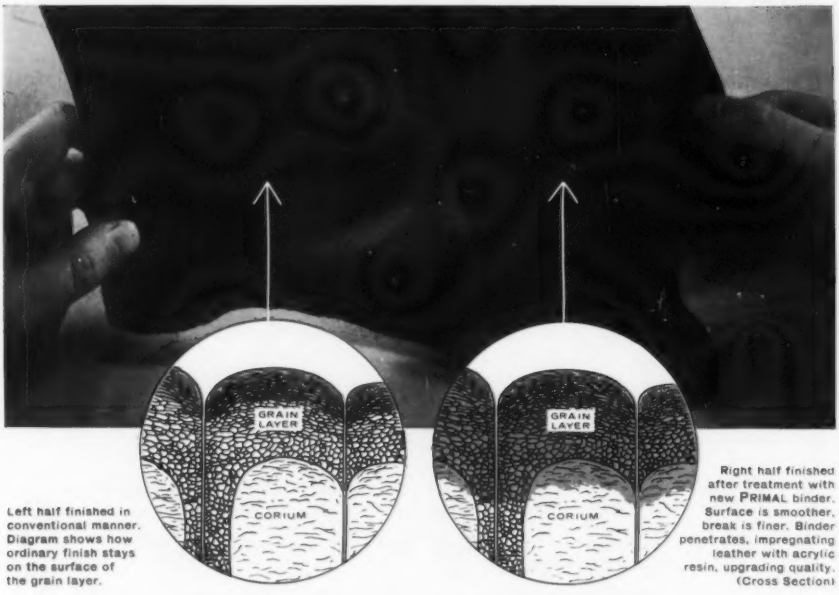

Left half finished in conventional manner. Diagram shows how ordinary finish stays on the surface of the grain layer.

Right half finished after treatment with new PRIMAL binder. Surface is smoother, break is finer. Binder penetrates, impregnating leather with acrylic resin, upgrading quality. (Cross Section)

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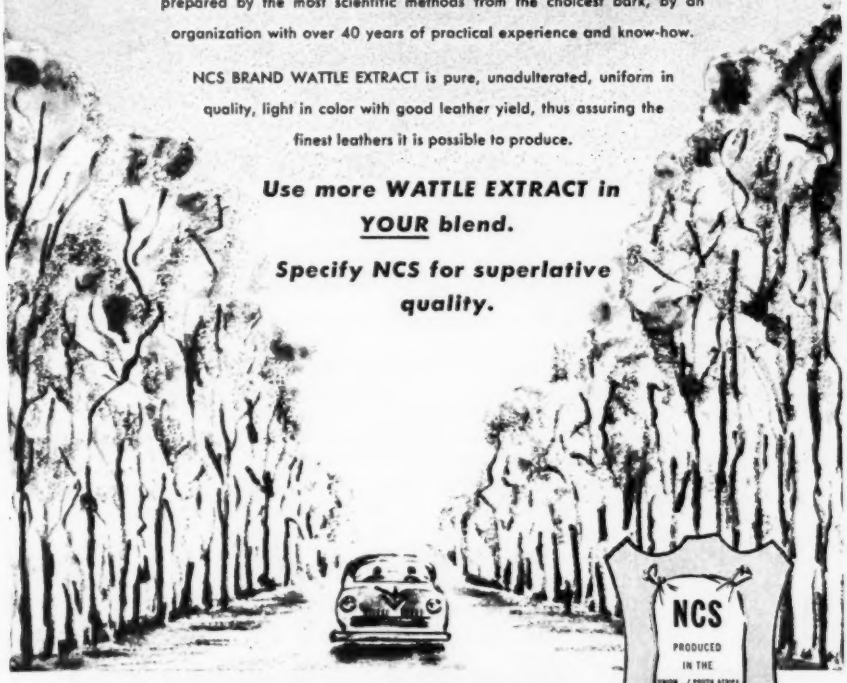

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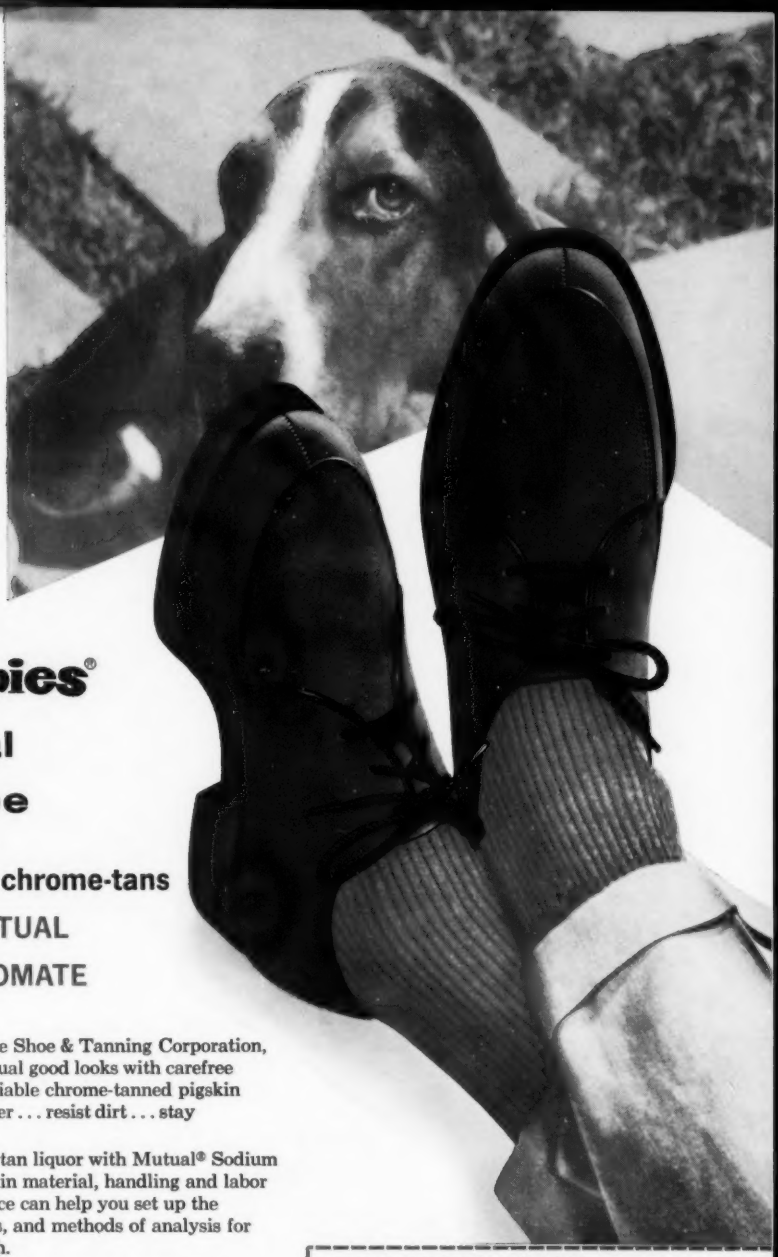

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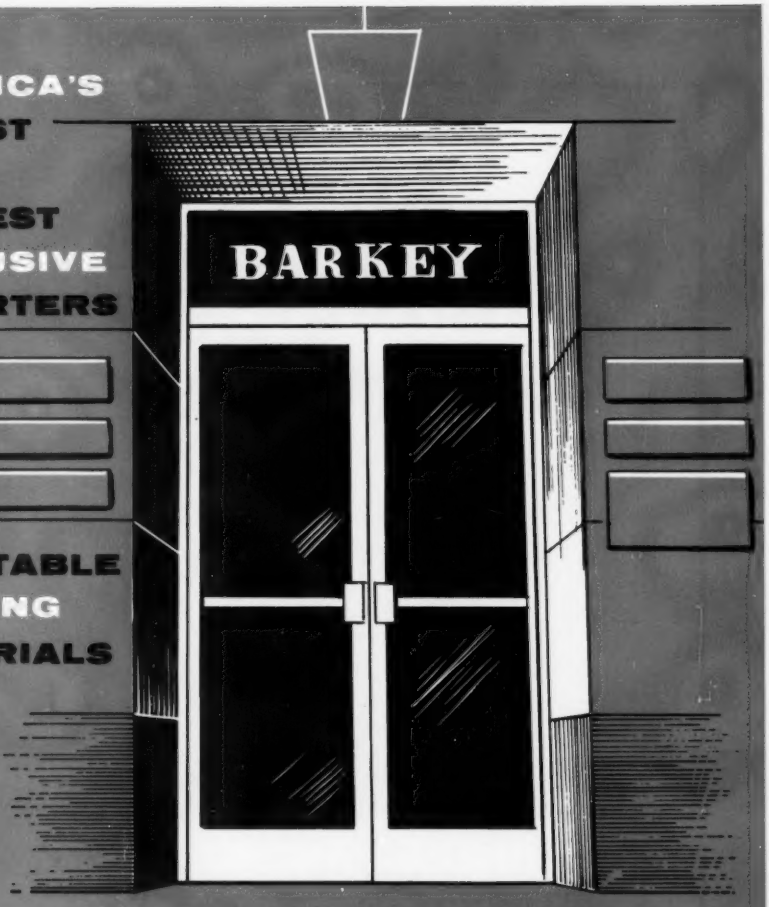

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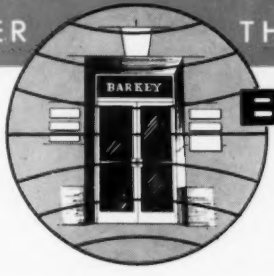

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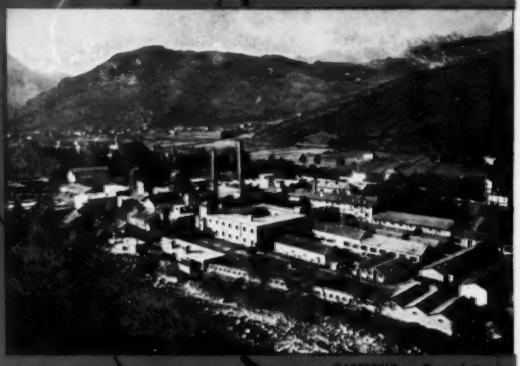

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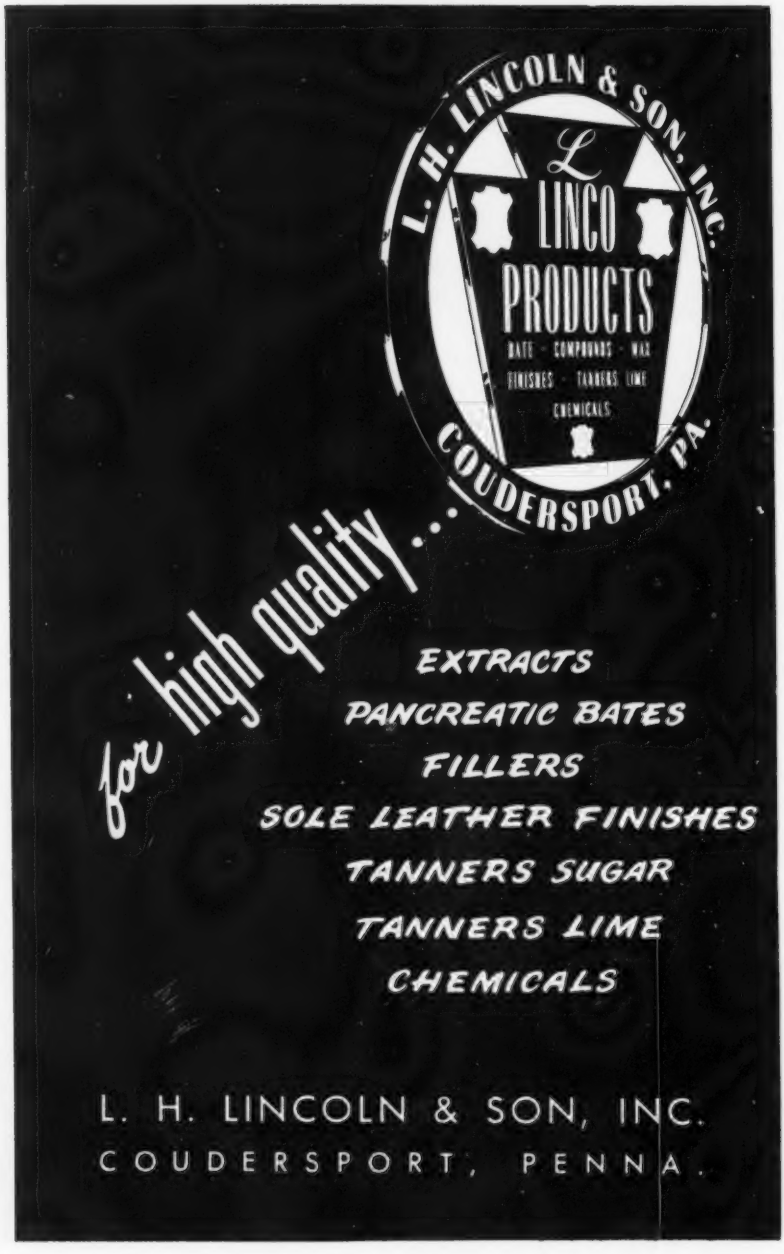
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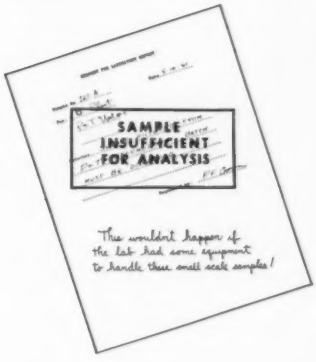
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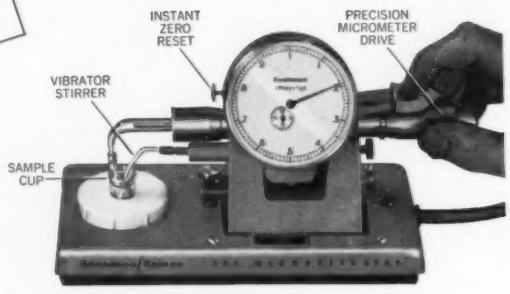

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General correspondence concerning the *Journal* should be mailed to the Managing Editor.

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EDITORIAL

The Journal of the American Leather Chemists Association *is glad to take this opportunity to welcome the International Union of Leather Chemists Societies to its first Congress in the United States. In honor of this meeting the staff of the* Journal *has arranged some special features as a modest commemoration of this important occasion.*

Emeritus Professor Donald Burton, honorary treasurer of the International Union and mutual member of the ALCA for nearly forty years, kindly consented to write a history of the International Union. Officers of the Union sent photographs and biographical sketches. Mr. Jerome S. Rogers, retired head of the Hides and Leather Laboratory of the Department of Agriculture and a member of the ALCA since 1912, wrote the history of our Association. Officers of the ALCA provided photographs and biographies. It seemed appropriate to include the recently arrived minutes of the 1959 International Union meeting.

From a scientific standpoint this issue is devoted to a manuscript by Dr. John H. Highberger entitled "Recent Advances in Knowledge of the Structure of the Collagen Fibril and of the Properties of the Tropocollagen Macromolecule". This is based upon the first John Arthur Wilson Memorial Lecture given by Dr. Highberger at the 1960 meeting of the ALCA. The address has been expanded and recent literature has been included. We are proud of the fact that a scientist who has been associated with leather chemistry for so many years, a member of our Association since 1926 and our president from 1942 to 1944, is now a world authority on the structure of collagen.

The transition of all of the world's leather chemists' societies and journals from analytical chemistry to applied and basic research is apparent. While analytical methods are important and, indeed, are still in need of improvement, the broadening of the base of leather chemistry has been desirable and fruitful. The stature of the leather chemist has kept pace, so that today he is both a supervisor of leather production and a research scientist. In fact, one can regret that there is not a closer

liaison between the academic worker on protein structure and the tanner. The pure scientist would find much of help in the everyday reactions of a tannery and would avoid some mistakes. In turn, the leather industry would profit from the association.

In spite of the tremendous increase in our knowledge during this century much remains to be done. The use of substitutes for leather is a constant challenge. Fundamentally, the strength of the leather industry resides in the structure of its raw material and the skill of the tanner. The unique combination of properties resulting from processing hides and skins into leather is not likely to be duplicated by synthesis. As only one phase of research, these physical and chemical properties need to be more carefully and thoroughly defined. They must be emphasized to the public in language that can be understood. That this is not an insuperable task is well illustrated by the success in promoting wool, another natural fiber. In addition, we have the constant and enduring advantage of the beauty and esthetic appeal of the genuine article.

The program for the Congress of the International Union of Leather Chemists Societies is of interest to everyone. It represents a nice balance between practical and theoretical subject matter. There are papers which range from the methods of chrome tanning to the structure of collagen. More than half of the program comes from abroad. The ALCA, as the host society, wishes to express its appreciation not only for these contributions to the program but also for the willingness of so many members of the International Union to make the long and expensive trip to attend the Congress. We are confident that your visit to the United States will be both pleasant and profitable. ALCA members will do their best to make it so. *W. W.*

THE INTERNATIONAL UNION OF LEATHER CHEMISTS SOCIETIES

EM-PROF. D. BURTON

Honorary Treasurer

The leather industry is outstanding for its international cooperation. In 1897 the International Association of Leather Trades' Chemists, known as the I.A.L.T.C., the I.V.L.I.C., the I.G.K.F., or the A.I.C.I.C., was formed with the object of adopting standard methods of analysis and uniting in research work. It published its Journal, *The Collegium*, and had Sections for England, Germany, Scandinavia, France, Belgium, Italy, Austria-Hungary, Spain, and the United States of America. After 1914 the international position rendered this cooperation impossible. In 1917 the Society of Leather Trades' Chemists (S.L.T.C.) was formed and became the International Society (I.S.L.T.C.) in 1925. The American Leather Chemists Association (A.L.C.A), which had been formed in 1903, and the *Collegium* were also in operation. At the conclusion of the Second World War it was clear that more effective progress would be obtained if each Section of the I.S.L.T.C. formed an autonomous Society and a federation of these individual Societies was formed. The London meeting of the Executive Committee of the I.S.L.T.C. in November, 1947, was historic. The following were present: Prof. Dr. P. Chambard (President), Mr. W. R. Atkin (Acting President), Dr. J. Gordon Parker (Hon. Secretary), Mr. A. Harvey (Acting Hon. Secretary), Prof. D. McCandlish (Hon. Treasurer), Dr. D. Burton, and by invitation Mr. C. R. Loos (Past President). It was decided that the I.S.L.T.C. should cease to function as such on December 31, 1947, and that the Australian, British, Indian, South African, and General Sections should form the Society of Leather Trades' Chemists effective January 1, 1948. A draft constitution for the formation of an International Union of Leather Chemists' Societies had been drawn up and the following Provisional Officers were elected: President —Prof. Dr. P. Chambard; 1st Vice-President—Mr. J. R. Blockey; 2nd Vice-

President—Mr. J. Mallebay; Hon. Treasurer—Mr. W. R. Atkin, who was succeeded by Dr. D. Burton in June, 1949; and Hon. Secretary—Mr. A. Harvey. Subscriptions for 1949 were paid by the American, Belgian, British, Dutch, French, Italian, and Swiss Member-Societies. The First Conference was held in Paris in September, 1949, under the Presidency of Prof. Dr. Chambard. At the Council of Delegates, representatives from America, Belgium, England, Finland, France, Holland, Italy, the Nordic Countries, and Switzerland were present. The Leather Chemists' Societies of Czechoslovakia and the Nordic Countries were admitted into the Union. Dr. H. G. Turley (U.S.A.) and Dr. K. H. Gustavson (Nordic) were co-opted as members of the Executive Committee. Later the Spanish Society was elected as member of the Union. The Second Conference was held in London in September, 1951, under the Presidency of Mr. J. R. Blockey, and the German Society was elected as a member. The following Conferences followed: Barcelona in 1953 (President—Mr. J. Mallebay), Stockholm in 1955 (President—Dr. K. H. Gustavson), Rome in 1957 (President—Dr. H. G. Turley) and, Munich in 1959 (President—Prof. Dr. G. A. Bravo). Following the grievous death of Mr. A. Harvey in April, 1957, Mr. G. Forsyth became the Hon. Secretary.

The Seventh Conference in Washington this year under the Presidency of Prof. Dr. W. Grassmann should be a memorable one because the Union now embraces American, Austrian, Argentinian, Belgian, British, Czechoslovakian, Dutch, Egyptian (U.A.R.), French, German, Hungarian, Indian, Italian, Nordic, Polish, Spanish, Swiss, Turkish, and Yugoslavian Member-Societies.

PROF. DR. W. GRASSMANN

President

Professor Dr. W. Grassmann, born in Munich in 1898, received his doctor's degree in 1923, submitting a thesis on proteolytic enzymes of plants. From 1923 to 1928 he did research work as assistant to Richard Willstäter in the field of enzymology in the university laboratory of Munich. From 1928 until 1934 he was occupied as "Privatdozent". Publications during this period included "Specifity of Peptidasis", "Activation and Inhibition of Enzymes", and "Constitution of Glutathion".

In 1934 Prof. Grassmann became director of the Kaiser-Wilhelm-Institut für Eiweiss- und Lederforschung in Dresden, an institute located since 1957 in Munich and now known as the Max-Planck-Institut für Eiweiss- und Lederforschung.

About 300 works have been published in the field of collagen and peptides research, tannins, and electrophoretic techniques by Professor Grassmann and his collaborators.

Professor Grassmann received the prize of the Verein für Gerbereichemie und Technik in 1957 and became a member in 1959 of the Bayrische Akademie der Wissenschaften.

P. J. van Vlimmeren, born in Dordrecht (Holland) on August 6, 1921, was graduated with distinction from the Technical University of Delft in 1946 with work on selective hydrogenation of unsaturated oils and the effect of chrome pretannage on the uptake of vegetable tannins by hide powder. Since 1946 he has been on the staff of the Dutch Leather Research Institute T.N.O. in Waalwijk where he is now head of the leather research and technical service department. He has published nearly 150 scientific papers and reports on various aspects of the leather industry.

IR. P. J. VAN VLIMMEREN
1st Vice-President

PROF. DR. GIUSEPPE A. BRAVO
2nd Vice-President

Professor Dr. Bravo, born in Turin, Italy, in 1897, earned his doctorate in chemistry at the University of Turin in 1920. Joining the Leather Institute in Turin as an assistant in 1923, he was promoted to professor in 1932. From 1939 to 1957 he was with FNET (Fabrica Nazionale Estratti Tannini) in Noncalieri. Since 1957 he has been with Ledoga in Milan. An abstracter for *Chemical Abstracts* for over 30 years, Dr. Bravo is president of the Italian Society of Leather Chemists and former president (1957-59) of the I.U.L.C.S.

DR. EDWIN J. BAUMANN
Executive Committee Member

Dr. Baumann lives in Switzerland, where he received his Diploma in Chemistry and Engineering and his Doctor's degree from the Federal Institute of Technology, Zurich. After two years with the Swiss Institute for Testing Materials in St. Gall he joined Bally's Shoe Factories Ltd., Schoenenwerd, in 1927, where he is still employed in the capacity of Research Director.

Dr. Baumann is particularly well known for his work in the listing and evaluation of shoe leather. Early in his career he recognized the need for dynamic methods that would reliably predict shoe wear, and over the years he has developed many such methods as well as related machines. Some of his methods are under consideration as standard methods by the I.U.L.C.S.

He has been an active member of ALCA since 1949 and has served two terms as president of the Swiss Leather Chemists Society.

MIETH MAESER
Executive Committee Member

Mieth Maeser, Past President of ALCA, is a graduate of Brigham Young University and Massachusetts Institute of Technology. He has been associated with the United Shoe Machinery Corporation for more than twenty years. Since becoming a member of ALCA in 1941, he has played an important role in devising, evaluating, and revising physical test methods for leather.

Professor Burton, M.B.E., Honorary Treasurer of the I.U.L.C.S. since 1949, was Assistant to Prof. H. R. Procter, when the Procter International Research Laboratory opened in 1914. After war service and practical experience, he acted as Chief Chemist to Wm. Walker & Sons Ltd. from 1925 to 1951. He received the D.Sc. degree from Leeds University in 1926, where in 1951 he was appointed Professor of Leather Industries and in 1955 Hon. Director of the Procter International Research Laboratory. He was retired in 1959 with the title of Emeritus Professor. Professor Burton is an Honorary Member of the City and Guilds of London Institute and a Mutual Member of ALCA (since 1922). He is perhaps best known for his work for the Society of Leather Trades' Chemists, having been Hon. Treasurer since 1923. In 1945, the Donald Burton Prize was established as a "mark of esteem and regard" to commemorate his work as President, and in 1959 he received the rare distinction of Honorary Membership.

EM-PROF. DONALD BURTON
Honorary Treasurer

GEORGE FORSYTH
Honorary Secretary

Mr. Forsyth studied leather manufacture at the University of Leeds from 1923 to 1926 and is now Chief Chemist to the Highfield Tanning Co. Ltd., Runcorn, England. President of the Society of Leather Trades' Chemists from 1952 to 1954, he is now a Convenor of the Society's Leather Analysis Committee. In 1957 he succeeded A. Harvey as Honorary General Secretary of the I.U.L.C.S.

BRIEF HISTORY OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

JEROME S. ROGERS

INTRODUCTION

In 1862 a law was passed in the United States making the Agricultural Division of the United States Patent Office an independent Department of Agriculture. In the years that followed, many and varied fields of study engaged the attention of the chemists in the Division of Chemistry of the Department of Agriculture. Among these were studies of the tannin content of several materials including oak, hemlock, and wattle barks, chestnut wood, canaigre roots, algarobilla and sumac leaves. The methods used for the determination of tannin varied. They included the methods of Hammer (1), Lowenthal (2), and F. Jean (3).

In 1880 agricultural chemical research and the analytical methods used were in a chaotic condition. English, French, and German methods of analysis were used by different chemists. Buyers' and sellers' chemists obtained different results, and there was wrangling and discord over analyses due to the lack of mutually adopted standard methods. To provide for the adoption of standard methods of analysis for the agricultural chemists, several meetings were called, and as a result, on September 9, 1884, the present Association of Official Agricultural Chemists (AOAC) was formed. During the next ten years the scope of the work of AOAC was expanded. Methods of analysis of various materials were studied and improved.

In 1893 several leather chemists were in attendance at the Columbian Exposition in Chicago. W. H. Krug was engaged in an investigation of foreign tanning materials. He used a method recommended by H. R. Procter (4) of England. This consisted of percolating the tannin solution through a column of hide powder and determining the solids remaining in the percolate after discarding the first 50 cc. From the difference between the solids before and after percolation, the tannin could be calculated. Krug and Collingwood were not satisfied with this method.

After discussing the need for a better method for tannin determination, Messrs. Krug, Collingwood, Hurty, and Westenfelder decided to call a meeting of leather chemists on October 30, 1893, in Chicago. Due to the distance involved, leather chemists from the East did not attend. Messrs. Krug, Hurty, Fiebing, and Westenfelder met and after careful consideration decided

to organize an Association of American Leather Chemists, and adopted a provisional method of tannin analysis.

Available information indicates that this group of leather chemists did not begin to function as a separate and distinct organization at that time. They, with other leather chemists, continued to meet with the AOAC and were largely responsible for the work done on methods of tannin analysis (5) in the Tannin Section.

Since the leather chemists were not actually employed in the Department of Agriculture, they could not be members of the AOAC and had no voice in the approval or rejection of the proposed methods for tannin analysis. It was the feeling of these chemists that only a very limited number of the members of AOAC were interested in or familiar with the methods of analysis for tanning materials or leather. Because of these conditions the tanning and leather chemists decided to form a separate Association of American Leather Chemists.

EARLY HISTORY

It was at the close of the Washington, D. C., meeting of the AOAC, November 22, 1903, that a group of about nine leather chemists met and officially organized the American Leather Chemists Association (ALCA). The names of all of those who participated in the organization meeting are not positively known, but George A. Kerr, H. C. Reed, and W. H. Teas are known to have been present. It is probable that some of the following were also there: T. J. Mosser, F. H. Small, W. K. Alsop, F. R. Mosbaugh, Robert P. Cushing, and H. T. Wilson. George A. Kerr was elected president, W. H. Teas vice president, and H. C. Reed secretary-treasurer. The objects of the association were the improvement and standardization of methods of analysis.

The First Annual Meeting of ALCA was held in St. Louis, Mo., September 26–28, 1904, in conjunction with the annual meeting of AOAC. The leather chemists presented committee reports on:

(a) Analyses of chestnut, quebracho, and hemlock extracts by the Association method.

(b) Study of causes of variations found in soluble solids and insolubles.

(c) Analyses of fresh and spent bark and fresh chestnut wood.

(d) Investigation of provisional methods for determining acid in yard liquors.

(e) Protecting solutions against evaporation during analysis.

A full quota of officers was elected to serve in 1905. They were:

President	W. H. Teas
Vice President	H. T. Wilson
Secretary-Treasurer	H. C. Reed
Referee on Tannin	H. C. Reed
Executive Committee	W. K. Alsop, F. H. Small, and George A. Kerr

The Second Annual Meeting of ALCA was held November 15–17, 1905, at Washington, D. C., again with the Tannin Section of AOAC. A committee was appointed to consider the advisability of publishing an ALCA journal in which the results of committee work could be reported and scientific papers could be published. The committee reported favorably, and in January, 1906, the first issue of the *Journal of the American Leather Chemists Association* was published with W. H. Teas as its editor.

This first issue of the *Journal* gave the President's 1905 address, reports of nine committees, and other items of interest. A description and an illustration were given of the Alsop Combination Evaporator and Dryer. This equipment has been used for many years for the evaporation and drying of tannin residues.

Another item of particular interest is the fact that John H. Yocum is credited with the development of the shake method for tannin analysis, which, with certain improvements, is in use today.

The Official Method of the ALCA for tannin analysis was first printed in the *Journal* in March, 1906. The method included analysis of crude materials, extracts, and liquors. On the analysis solution, total solids, soluble solids, and nontannins were determined. The nontannin determination was made by shaking the analysis solution with washed, chromed hide powder, filtering, and evaporating an aliquot of the filtrate.

At the Third Annual Meeting, held in New York City, November 22–23, 1906, the ALCA met for the first time as a separate and distinct organization. The suggestion by W. H. Teas, the Editor, that the *Journal* would be more valuable to its readers if it contained abstracts from other tanning and leather chemistry journals was approved, and abstracts and patents have been a regular feature of the *Journal* since January, 1907.

The Fourth Annual Meeting of ALCA was held in Chicago, August 29–31, 1907, during the week of the Leather Market Fair. In commenting on W. W. Skiddy's address before the meeting, Dr. J. Gordon Parker of London said

that the new International Association of Leather Trades Chemists' method of tannin analysis, which became their official standard method on September 1, 1907, was practically the ALCA method. This gave excellent recognition to the accomplishment of the American Leather Chemists in developing a more accurate method for tannin determination.

At the Fifth Annual Meeting of the Association, held in Boston, November 12–14, 1908, a proposal was approved to change the by-laws, making the terms of office of the president, vice president, and secretary-treasurer two years. Official ALCA methods for tannin analysis and provisional methods for sampling tanning materials and the analysis of leather were published.

AFFAIRS OF ALCA OVER THE YEARS

The first five years of ALCA having been successfully completed, the Association became established on a permanent basis and was recognized at home and abroad as a dependable organization engaged in the development of methods of analysis for the leather industry. From this point on are reviewed some of the highlights of the Association, its *Journal*, its members, and its broader accomplishments in the field of chemistry as applied to tanning and leather.

In 1909 A. D. Little called attention to the deteriorating effect on leather of the sulfur fumes from illuminating gas and referred to Dr. J. Gordon Parker's experiments exposing leather to the fumes of burning gas with the result that the leather was completely destroyed (6). During the same year ALCA went on record as favoring the foundation of a tanners' research laboratory and as ured the National Association of Tanners of their interest and cooperation.

In April, 1910, W. H. Teas resigned as Editor of the *Journal*. He had served effectively since its first issue in 1906. The Council appointed W. K. Alsop to fill his place as Editor and Business Manager.

The Seventh Annual Meeting of ALCA was held in Chicago, October 6–8, 1910, in conjunction with the National Association of Tanners. At this meeting the National Association of Tanners voted to establish a tanning school as a department of Pratt Institute.

In October, 1915, a committee of the National Association of Tanners presented a plan for the establishment of a Tanners' Research Laboratory, the control to be in the hands of a joint committee of the National Association of Tanners and the ALCA (7). The funds required were obtained in the fall of 1916, and the laboratory was established with J. B. Churchill as director in the fall of 1917 in Pratt Institute.

During 1917 the ALCA council authorized the preparation and printing of the first 10-year index for the *Journal*. By this time the activities of ALCA had been expanded far beyond methods of analysis, and John Arthur Wilson proposed, and it was unanimously approved, that the Association by-laws be amended as regards its objects to read: "The objects of this Association are (*a*) to devise and perfect methods of analysis of leathers and of all materials used in their manufacture, (*b*) to promote the advancement of chemistry, especially in regard to problems confronting the leather industries, and (*c*) to publish the results of investigations and research dealing with the above subjects." Another amendment to the by-laws, which provided for active, associate, and mutual members, was approved.

In 1920 the ALCA Council decided that the hide powder supplied to ALCA members by the Standard Manufacturing Company of Ridgway, Pa., should be recognized as the Official Hide Powder for use by ALCA in tannin analysis after it had been approved by the ALCA Hide Powder Committee.

During the years of World War I, the affairs of ALCA had not prospered as well as might be desired, and the Council and members felt that 1920–22 were critical years for ALCA. They felt that the election of F. H. Small as president would give the experienced guidance needed. F. H. Small was accordingly elected. This is the only case in the history of the ALCA in which a man has been elected a second time to the presidency.

The American Leather Research Laboratory for its first three years was maintained in New York by the Tanners' Council. Its first director was J. B. Churchill. He was followed by George L. Terrassee. In 1921 the Research Laboratory was moved to the University of Cincinnati and placed under direction of Dr. George D. McLaughlin. The first results of Dr. McLaughlin's research appeared in the 1921 ALCA *Journal*, June and August issues.

In 1922 the ALCA for the first time held its Annual Meeting outside of the United States. This, the 19th Annual Meeting, met at Bigwin Inn, Bigwin Island, Canada. F. H. Small, the retiring President, reported that the Association was sound and healthy, both numerically and financially. The confidence placed in Mr. Small's leadership through the critical period was thus justified. At this meeting further evidence of the value of the Tanners' Council Research Laboratory was given by the research paper presented by Dr. McLaughlin on the science and practice of curing heavy hides.

In 1923 the Council decided to publish the ALCA methods in a loose-leaf booklet, thus making it possible to make changes and additions without reprinting all the methods.

The year 1924 marked a new era in the history of Leather Chemistry in the United States. On November 19, the Tanners' Council of America, in a

dignified ceremony, presented to the University of Cincinnati the new building—a laboratory designed exclusively for research in tanning and leather chemistry (8).

In the election of officers at the 25th Annual Meeting in 1928 Dr. Thomas Blackadder and Dr. Lloyd Balderston received a tie vote. This is the only time that a tie vote for President in ALCA has occurred. It was necessary to hold a later election. This resulted in the election of Dr. John Arthur Wilson as President. In December of that same year, 1928, Dr. John Arthur Wilson delivered the Chandler Lecture at Columbia University and received the Chandler Medal in recognition of his application of modern concepts of chemistry to the making of leather. The title of his lecture was "Chemistry and Leather" (9).

In 1930 the ALCA Council authorized Dean Williams, Associate Editor of the *Journal*, to complete the second 10-year index. This was completed and available in 1931. It is unfortunate for leather workers and the *Journal* that subsequent 10-year indexes have never been assembled.

In 1931 John Arthur Wilson received the Nichols Award for outstanding achievements in Leather, Sanitation, and Colloid Chemistry.

In 1933 at the 30th Annual Meeting of the ALCA, Dr. Edmund Stiasny, Director of the Tanning School at Darmstadt, Germany, gave a lecture on "Our Present Knowledge of the Chemistry of Chrome Tanning."

In 1936 the ALCA Council appointed an Editorial Board to review and pass on papers submitted to the *Journal* for publication. W. K. Alsop, who had been Editor of the *Journal* from 1910 to 1936, died on January 5, 1936. Dean Williams was appointed Editor.

H. C. Reed, Secretary-Treasurer of ALCA, offered his resignation after 26 years of faithful service to the Association. C. A. Blair was elected secretary-treasurer.

It was suggested that the ALCA should be incorporated. This action was approved by the Council and by vote of the Association in 1937.

At the annual meeting in 1939 Mr. B. A. Schiller, chairman of the Business Committee, was presented with the first William K. Alsop Memorial Award in recognition of the substantial assistance rendered by him and members of his committee in connection with the financial affairs of the Association.

In 1940 a major revision of ALCA by-laws was passed by vote of the Association (10). This revision organized and expanded the by-laws and modified the objects of the Association to read as follows:

> "To devise and perfect methods for the analysis and testing of leathers and all materials used in connection with their manufacture.

"To promote the advancement of Chemistry and other sciences, especially in regard to their application to the problems confronting the leather industry.

"To publish the results of investigations and researches dealing with the above subjects.

"To advance the professional welfare of its members by all legitimate means."

It provided for an executive secretary appointed by the Council to be a paid officer of the Association.

It eliminated alternative methods of analysis except when new methods are under trial.

Classification of members was changed to include active, associate, life, honorary, and mutual members.

H. C. Reed, charter member, Past President, and Secretary-Treasurer from 1908 to 1936, died on July 10, 1940.

In 1942 the Association approved an amendment to the by-laws to become effective in the election of officers in 1946 and every two years thereafter. This amendment eliminated the office of Vice-President and replaced it by the office of President-Elect. This change meant that the duties formerly assigned to the Vice President were assumed by the President-Elect, and that two years after his election as President-Elect he automatically became President of the Association.

In 1944 Dr. Fred O'Flaherty, the Director of the Tanners' Council Research Laboratory, was elected Secretary-Treasurer of the Association. Mr. C. A. Blair, the former Secretary-Treasurer, had advised before the election that he could no longer serve in that capacity.

In 1945 the Office of Defense Transportation refused the request of ALCA to hold its annual meeting in Cincinnati, Ohio. Later two sectional meetings to replace the annual meeting were permitted. One was held in Milwaukee, Wisconsin, and the other in New York City.

On January 24, 1947 the ALCA Council voted to give Dr. E. R. Theis $2500 for the purchase of research equipment to be used at Lehigh University in connection with leather and tanning research. At the same meeting $2500 was given to the Tanners' Council Research Laboratory, located at the University of Cincinnati in the Department of Applied Science in Tanning Research.

In 1948, at the 44th Annual Meeting, the Association voted to establish, at the University of Cincinnati, a Stiasny Fellowship. It was awarded to Miss Greta Karlsson, a former student and associate of Dr. Stiasny.

Upon the invitation of the International Union of Leather Chemists Societies and by the action of Council at their February 17, 1949, meeting, the ALCA became a member of the International Union. This membership continues and has led to a broader outlook for American leather chemists, an increasing attendance at international meetings, and the formation of many new friendships. It culminates in the present meeting in the United States, which is the first international meeting of leather chemists ever held in this country.

The 46th Annual Meeting was held at French Lick Springs Hotel, French Lick, Indiana, May 31–June 2, 1950. A. H. Winheim, the retiring President of ALCA, after completing a successful meeting, was killed in an automobile accident as he and Mrs. Winheim were on their way home.

The Committee on Tannin Analysis, after comparing the use of the Alsop combined evaporator and dryer with the Precision Scientific Company's Freas mechanical convection oven, recommended that the Freas oven be allowed as an alternate oven for tannin analysis.

The Golden Anniversary of ALCA was celebrated at the Annual Meeting held at Cincinnati, Ohio, June 7–10, 1953. During the Anniversary Banquet, the President, Dr. Turley, reported that the Association had received congratulations and greetings from the American Chemical Society and from the Leather Chemists Societies of New Zealand, South Africa, Switzerland, Italy, France, Spain, Free China, England, and the International Union of Leather Chemists Societies. Dr. Linus Pauling, a Nobel Prize winner, was the guest speaker.

The ALCA Award was established by Council in 1954. The sum of $1,000 is awarded to a member for the delivery of a meritorious paper at the Congress of the International Union of Leather Chemists Societies. The first recipient was Dr. Joseph R. Kanagy in 1955, followed by Dr. Rubin Borasky in 1957 and Dr. Lee P. Witnauer in 1959.

Dean Williams passed away on August 14, 1955. He was Associate Editor of the *Journal* for 13 years from 1923 to 1936 and Editor for 19 years from 1936 until his death. Mr. Ralph H. Twining, his assistant, became Acting Editor. In January, 1956, Council introduced a new system by creating the positions of Editor-in-Chief and Managing Editor. The term of the Editor-in-Chief is three years, and he cannot be reappointed to succeed himself. Dr. Henry B. Merrill became the new Editor-in-Chief and served with distinction from March 1, 1956, to March 1, 1959. He was succeeded by the present Editor-in-

Chief, Dr. Wallace Windus, whose term expires on March 1, 1962. Dr. Thomas C. Thorstensen and Professor Earl J. Watt, Lowell Technological Institute, have served continuously as Associate Editor and Managing Editor, respectively. The Editorial Board was expanded and has helped substantially to evaluate the increasingly complex and diverse manuscripts.

In 1956, at the 52nd Annual Meeting, the ALCA approved the formation of a joint committee with the American Society for Testing Materials to study the harmonizing and joint adoption of Physical Test Methods for Leather.

In 1957 the ALCA Physical and Mechanical Properties Committee on leather was organized. No subcommittees were formed, but most committee members were chairmen of committees or sections of the ALCA-ASTM Joint Committee on Leather.

The ALCA Council, at its June 14, 1959, meeting at Mackinac Island, Michigan, accepted the offer of Salem Oil and Grease Company to establish a John Arthur Wilson Memorial Lecture. In their meeting June 17 it was decided that a committee to select the Honor Lecturer would be composed of one member appointed by Salem Oil and Grease Company and two members appointed by the ALCA President, with one of these being a Council member. The first of these memorial lectures was delivered at the 56th Annual Meeting at Lake Placid, New York, June 19–22, 1960, by Dr. John H. Highberger. His lecture dealt with the elucidation of the structure of collagen.

It will be recalled that at the first annual meeting of ALCA reports were given by nine committees on the results of their studies on improvement of the methods of analysis. Work of this nature has continued each year. Much progress has been made but the work is never done. This is evidenced by the technical committee work reported at the annual meeting in 1960. There were nine committees reporting: Hide Powder, Raw Stock Evaluation, Mineral Leather, Tannin Analysis, Standards and Specifications, Vegetable Leather, Physical and Mechanical Properties, Preparatory and Posttanning Processes, and Tannery Effluents.

The International Union of Leather Chemists Societies has accepted the invitation of the ALCA to hold its next Congress in the United States, with the ALCA acting as host society. It is scheduled to be held August 20–25, 1961, at the Shoreham Hotel in Washington, D. C.

THE ALCA *JOURNAL*

The *Journal* has been published monthly without interruption for more than 55 years. The five editors have been capable and devoted men. At present the tenure of office is set at 3 years.

Through the years the *Journal* has published a wealth of committee reports dealing with methods of analysis, tanning materials, vegetable and chrome tanning processes, and leather service tests as well as an excellent coverage of abstracts from foreign leather journals and reviews of patents.

Of major importance are the multitude of theoretical and fundamental research papers that have been published. These have dealt with the principal phases in the development of our fundamental knowledge as related to hides, collagen, and the theories of tanning and leather formation. These papers have been furnished mostly by research laboratories and individual researchers. Due to the pressure of company work the tannery chemist seldom has sufficient time to conduct the type and amount of orginal research that he would wish to do.

ALCA MEMBERSHIP

From a beginning of about nine active members in 1903, the membership growth in some periods has been quite rapid. In war periods and times of depression the growth became irregular and in some cases decreased for a short time.

It is interesting to note in the tabulation below (11) how ALCA had spread its sphere of influence by 1955 by disseminating through its *Journal* knowledge on tanning and leather research to its members in 32 foreign countries and Canada.

	United States Members	U. S. States Represented	Foreign Members	Foreign Countries Represented	TOTAL
Active	428	26	75	24	503
Associate	294	23	48	22	342
Mutual	—	—	169	10	169
Student	—	—	1	1	1
	722		293		1015

The changes in the membership over the years and the present memberships (May, 1961) for each class of members are shown in the graph on page 416.

57 CONVENTIONS

AMERICAN LEATHER CHEMISTS ASSOCIATION

Meetings	Date	Hotel	Place	President	Term of Office
Organization	Nov. 22, 1903		Washington, D. C.	Geo. A. Kerr	Nov. '03–Sept. '04
1	Sept. 26–27, 1904	Inside Inn	St. Louis, Mo.	W. H. Teas	Sept. '04–Nov. '05
2	Nov. 15–, 1905	Normandy Inn	Washington, D. C.	H. C. Reed	Nov. '05–Dec. '06
3	Nov. 22–23, 1906	Grand Union	New York, N. Y.	J. H. Yocum	Jan. '07–Dec. '07
4	Aug. 29–31, 1907	Lexington	Chicago, Ill.	F. H. Small	Dec. '07–Dec. '08
5	Nov. 12–14, 1908	Brunswick	Boston, Mass.	H. T. Wilson	Dec. '08–Nov. '09
6	Dec. 2–4, 1909	Raleigh	Washington, D. C.	H. T. Wilson	Dec. '09–Nov. '10
7	Oct. 6–8, 1910	LaSalle	Chicago, Ill.	Jos. H. Russell	Nov. '10–Nov. '11
8	Dec. 7–9, 1911	Raleigh	Washington, D. C.	F. P. Veitch	Nov. '11–Dec. '11
9	Dec. 5–7, 1912	Raleigh	Washington, D. C.	F. P. Veitch	Dec. '11–Dec. '12
10	Dec. 4–6, 1913	Traymore	Atlantic City, N. J.	W. K. Alsop	Dec. '12–Dec. '13
11	Oct. 28–31, 1914	Sherman	Chicago, Ill.	W. K. Alsop	Jan. '14–Nov. '14
12	May 27–29, 1915	Marlborough Blenheim	Atlantic City, N. J.	L. E. Levi	Nov. '14–June '15
13	June 1–3, 1916	Marlborough Blenheim	Atlantic City, N. J.	L. E. Levi	June '15–July '16
14	June 7–9, 1917	Marlborough Blenheim	Atlantic City, N. J.	C. R. Oberfell	July '16–July '17
15	May 15–18, 1918	Ambassador	Atlantic City, N. J.	C. R. Oberfell	July '17–July '18
16	May 22–24, 1919	Marlborough Blenheim	Atlantic City, N. J.	R. W. Griffith	July '18–July '19
17	May 27–29, 1920	Marlborough Blenheim	Atlantic City, N. J.	R. W. Griffith	July '19–July '20
18	June 9–11, 1921	Ambassador	Atlantic City, N. J.	F. H. Small	July '20–July '21
19	June 21–23, 1922	Bigwin Inn	Canada	F. H. Small	July '21–Aug. '22
20	June 7–9, 1923	Greenbrier	White Sulphur Springs, W. Va.	C. C. Smoot, III	Aug. '22–July '23
21	June 18–20, 1924	Monmouth	Spring Lake, N. J.	C. C. Smoot, III	July '23–July '24
22	June 3–5, 1925	Traymore	Atlantic City, N. J.	J. S. Rogers	July '24–July '25
23	June 2–4, 1926	Traymore	Atlantic City, N. J.	J. S. Rogers	July '25–July '26
24	June 15–17, 1927	Univ. of Cincinnati	Cincinnati, Ohio	Lloyd Balderston	July '26–Oct. '27
25	June 6–8, 1928	New Ocean House	Swampscott, Mass.	Lloyd Balderston	Oct. '27–Oct. '28
26	June 5–7, 1929	Chateau Frontenac	Quebec, Canada	John Arthur Wilson	Oct. '28–July '29
27	June 18–20, 1930	Schroeder	Milwaukee, Wis.	John Arthur Wilson	July '29–July '30
28	May 27–29, 1931	Traymore	Atlantic City, N. J.	R. W. Frey	July '30–June '31

Meetings	Date	Hotel	Place	President	Term of Office
29	May 26–28, 1932	Traymore	Atlantic City, N. J.	R. W. Frey	June '31–July '32
30	June 7–9, 1933	Claridge	Atlantic City, N. J.	Geo. D. McLaughlin	July '32–July '33
31	May 23–25, 1934	Skytop Lodge	Skytop, Pa.	Geo. D. McLaughlin	July '33–July '34
32	June 12–14, 1935	Skytop Lodge	Skytop, Pa.	Fred O'Flaherty	June '34–July '35
33	June 12–14, 1936	Skytop Lodge	Skytop, Pa.	Fred O'Flaherty	July '35–July '36
34	June 8–11, 1937	Royal York	Toronto, Canada	A. C. Orthmann	July '36–July '37
35	June 14–17, 1938	Bedford Springs	Bedford, Pa.	A. C. Orthmann	July '37–July '38
36	June 5–8, 1939	Buckwood Inn	Shawnee, Pa.	H. B. Merrill	July '38–July '39
37	May 27–29, 1940	Sagamore	Lake George, N. Y.	H. B. Merrill	July '39–Aug. '40
38	June 23–25, 1941	Sagamore	Lake George, N. Y.	V. J. Mlejnek	Aug. '40–July '41
39	June 1–2, 1942	Deshler-Wallick	Columbus, Ohio	V. J. Mlejnek	July '41–July '42
40	June 2–3, 1943	Statler	Buffalo, N. Y.	J. H. Highberger	July '42–July '43
41	May 29–31, 1944	Pennsylvania	New York, N. Y.	J. H. Highberger	July '43–July '44
2 Sectional Meetings	Oct. 17, 1945	Pfister	Milwaukee, Wis.	Dean Williams	July '44–July '45
	Oct. 31, 1945	Pennsylvania	New York, N. Y.	" "	" "
42	June 19–21, 1946	Sagamore	Lake George, N. Y.	Dean Williams	July '45–July '46
43	June 19–21, 1947	Edgewater Beach	Chicago, Ill.	T. F. Oberlander	July '46–July '47
44	June 17–19, 1948	Mt. Washington	Bretton Woods, N.H.	T. F. Oberlander	July '47–July '48
45	June 22–24, 1949	Monmouth	Spring Lake, N. J.	A. H. Winheim	July '48–July '49
46	May 31–June 2, 1950	French Lick Springs	French Lick, Ind.	A. H. Winheim	July '49–July '50
47	June 11–13, 1951	Griswald	Groton, Conn.	R. M. Koppenhoefer	July '50–July '51
48	June 1–4, 1952	New Ocean House	Swampscott, Mass.	R. M. Koppenhoefer	July '51–July '52
49	June 7–10, 1953	Netherland-Plaza	Cincinnati, Ohio	H. G. Turley	July '52–July '53
50	June 6–9, 1954	Bedford Springs	Bedford, Pa.	H. G. Turley	July '53–July '54
51	May 22–25, 1955	New Ocean House	Swampscott, Mass.	Edwin S. Flinn	July '54–July '55
52	June 17–20, 1956	Grand	Mackinac Island, Mich.	Edwin S. Flinn	July '55–July '56
53	June 2–5, 1957	Lake Placid Club	Lake Placid, N. Y.	E. B. Thorstensen	July '56–July '57
54	May 25–28, 1958	New Ocean House	Swampscott, Mass.	E. B. Thorstensen	July '57–July '58
55	June 14–17, 1959	Grand	Mackinac Island, Mich.	Mieth Maeser	July '58–July '59
56	June 19–22, 1960	Lake Placid Club	Lake Placid, N. Y.	Mieth Maeser	July '59–July '60
57	Aug. 20–25, 1961	Shoreham	Washington, D. C.	Reuben Henrich	July '60–July '61

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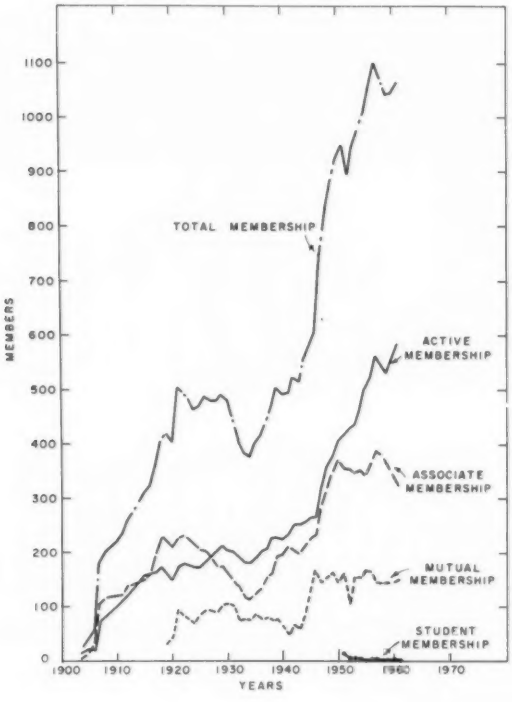

DR. REUBEN G. HENRICH
President

Dr. Henrich received his B.S. degree from Carroll College and his M.S. and Ph.D. degrees from the University of Wisconsin. After three years (1929–32) as a chemist with A. Gallun & Sons, Milwaukee, he did research and development work with John Arthur Wilson from 1932 to 1935. His next 17 years were spent in research, development, and production in the Surpass Leather Co., Philadelphia. In 1954 he joined the B. D. Eisendrath Tanning Co. of Racine, Wisconsin, as Production Manager, leaving that firm in June, 1959, to go with Hiteman Leather Co., West Winfield, N. Y.

An ALCA member since 1930, Dr. Henrich has participated actively in the Association, serving on numerous committees and on the Council prior to his election as President.

DR. ROBERT STUBBINGS
President-Elect

Dr. Stubbings is presently Director of the Institute of Leather Technology of the Milwaukee School of Engineering. He received his education at Lehigh University—B. S. Chem 1941, M. S. Chem 1946, Ph.D. Chem (Physical Chemistry major) 1949. During his graduate work he studied under the late Edwin R. Theis and thus was introduced to leather chemistry and technology. Following the death of Dr. Theis in 1953, Dr. Stubbings was appointed as Director of the Leather Institute at Lehigh University. In 1960 the Institute moved to the Milwaukee School of Engineering as part of a new program for cooperative research with industry inaugurated at MSOE. His major interests are the development of control and measuring devices for the leather industry as well as problems dealing with the chemical technology of leather processing.

DR. FRED O'FLAHERTY
Secretary-Treasurer

Dr. O'Flaherty received his M.D. degree from Eclectic Medical College, Cincinnati, in 1926 and his M.D.V. from the Cincinnati College of Veterinary Medicine. A member of the faculty at the University of Cincinnati since 1924, he has been successively research assistant, research associate, research director (1924-31) and professor in basic science (1931 to date). He has also been the executive director of the Research Foundation since 1946. Dr. O'Flaherty is an active member of the ALCA (President 1935-37 and Secretary-Treasurer since 1944), Live Stock Conservation, Inc. (President 1953-55), A.A.A.S., and Sigma Xi.

MEETINGS OF THE COUNCIL OF DELEGATES I. U. L. C. S.

FIRST MEETING

Kleine Kongresshalle, Munich
September 7, 1959

Present.—In the Chair, Prof. G. A. Bravo. Members of the Executive Committee and 43 delegates.

Minutes.—The minutes of the previous meeting (Rome, Sept. 16, 1957) having been circulated were taken as read.

Honorary Secretary's Report.—As the result of a postal ballot, the Polish Leather Chemists Society had been admitted to the Union. By the same means the New Statutes had been adopted by a vote of 40 in favour and 5 against. On the question of postal ballots, it was reported that considerable difficulty was caused by Member-Societies not replying to letters; this caused not only inconvenience but delay and some increase in expense to the Union. Applications from Argentina, Egypt, and Hungary had been received. The new Joint I.C.T.-I.U.L.C.S. Committee met in London, March 19, 1958. The following points are left with the Union for consideration and comment:

1. A ready means of testing the wear of *boots and shoes.*
2. Eradication of the warble fly.
3. Uses for green fleshes to eliminate waste.
4. Improvements in leather quality.
5. Effect of substitute soling materials on the life of uppers.

An attempt is being made to set up a system of exchange of abstracts between Member-Societies.

In the discussion that followed it was agreed that it was desirable that the joint I.C.T.-I.U.L.C.S. Committee should meet at least once a year and report to the Member-Societies and that a meeting of editors and scientific publications should be held immediately after this meeting of Council of Delegates.

Honorary Treasurer's Report.—Prof. Burton read the financial statement and pointed out that although there was a balance of £850, the expenditure was increasing yearly. There was a considerable increase in the cost of the work of the Commissions, some of which was being paid for by various Member-Societies. He felt that these expenses should be borne by the Union and recommended that the subscription should be increased to meet this extra expenditure.

In the discussion that followed an increase in subscription from £6 (the original subscription) to £10 was suggested.

SECOND MEETING

Kleine Kongresshalle, Munich

September 11, 1959

Present.—In the Chair, Prof. G. A. Bravo. Members of the Executive Committee and 45 delegates.

Subscription 1960/1961.—On the proposition of the Treasurer, an increased subscription of £10 was unanimously approved. A motion put forward that the increase in income should be reserved for the work of the Commissions was defeated.

Election of Officers.—At the end of 1959, the President (Prof. G. A. Bravo) automatically becomes 2nd Vice President. Two nominations for 1st Vice President were received, Sig. Paniker de Pelach and Ir. P. J. van Vlimmeren. Van Vlimmeren was elected. There were only two nominations made for "Elected Members", Dr. E. Baumann and Dr. Y. Nayudamma. The Honorary Secretary and Treasurer not being due for re-election until 1961, the composition of the new Executive Committee becomes:

President	Prof. Dr. W. Grassmann
1st Vice President	Ir. P. J. van Vlimmeren
2nd Vice President	Prof. Dr. G. A. Bravo
Elected Members	Dr. E. Baumann
	Dr. Y. Nayudamma*
Hon. Treasurer	Prof. D. Burton
Hon. Secretary	Geo. Forsyth

To comply with the new Statutes (Article X) it was necessary to nominate assistants to the posts of Treasurer and Secretary. Prof. A. Ward and Mr. D. Tudor were respectively nominated.

*Dr. Nayudamma later resigned, and M. Maeser was appointed to fill his position.

1961 Conference.—There being no invitation for the 1961 Conference, on the recommendation of the Executive Committee it was unanimously approved that the possibilities of holding the next Conference in America should be explored.

New Members.—Applications from the Asociation Argentina de los Quimicis y tecnicos de la Industria del Cuero, the Society of Leather Trades Chemists and Technicians, Cairo, and the Hungarian Leather Trades Chemists Scientific Association had been received, and all complied with the necessary requirements. Their admission was unanimously approved. A late request for admission was received from the Turkish Society of Leather Chemistry and Industry. It was decided that if on translation their Statutes met with the necessary requirements, the admission of that Society be left to the discretion of the Secretary.

Commissions.—The Fastness Testing Commission expenses were so high that it had necessitated approaching Member-Societies for funds. It was agreed that an attempt should be made to keep these expenses at a level that could be met by the Union.

At the request of the French Society a new Commission will be set up to investigate the Sampling of Vegetable Tanning Materials. France is to nominate the Chairman of the Commission.

I.S.O.—It was agreed that it would be advantageous for the various Commissions, whenever possible, to become affiliated with the International Standards Organization.

Council of Delegates.—A proposition was made that the Executive Committee should always make recommendations to the Council for candidates for the two elected members of the Executive Committee.

Abstract Service.—The meeting of editors of scientific publications had agreed to an exchange of abstracts between the various Member-Societies. These abstracts would be circulated through the Hon. Secretary.

Appointment of Delegates.—As there are no records of the number of members in each Member-Society and as it was difficult to get this information through the medium of the post, a delegate from each Member-Society was requested to take, fill up, and return to the Secretary a form provided for this purpose.

THE FIRST JOHN ARTHUR WILSON MEMORIAL LECTURE*

RECENT ADVANCES IN KNOWLEDGE OF THE STRUCTURE OF THE COLLAGEN FIBRIL AND OF THE PROPERTIES OF THE TROPOCOLLAGEN MACROMOLECULE†

JOHN H. HIGHBERGER

Research Division
United Shoe Machinery Corporation
Beverly, Massachusetts

INTRODUCTION

I should like to begin by expressing to the Selection Committee of the Council, and to the sponsors of this lecture series, my deep appreciation of the honor they have conferred on me in selecting me to give the first John Arthur Wilson Memorial Lecture. It is fitting that Wilson's memory should be perpetuated by the establishment of such a series; no other American leather chemist has made so many important contributions to our knowledge of the scientific phenomena on which the processes of leather making are based—the importance of many of which, indeed, far transcends the bounds of leather science itself.

Wilson's many interests encompassed the field of protein structure. Introduced to this when it was in an embryonic state of development, during his early work with Proctor on the swelling of gelatin, he came to realize the vital importance to tanning technology of an increased knowledge of the structure of collagen. He became, in fact, one of the pioneers in the application of hydrogen bond theory to the structural problems presented by this protein.

In the eighteen years since his death much progress has been made in this field, and it seems appropriate that in this first Memorial Lecture I should attempt to survey our position as of today with respect to our understanding of the structure of the collagen fibril and the properties of the molecular unit of collagen.

*Presented June 20, 1960, at Lake Placid, N. Y. at the Fifty-sixth Annual Meeting of ALCA.

†The original work described in this paper was supported in part by research grant A-2632 from the National Institute of Arthritis and Metabolic Diseases.

THE FINE STRUCTURE OF THE COLLAGEN FIBRIL

Our present knowledge of the fine structure of the collagen fibril has been arrived at by a synthesis of the results of X-ray diffraction, electron microscopy, and the chemical examination of the types of amino acids of which it is composed and of the sequences in which these are arranged. In 1942, the year of Wilson's death, it had been recognized for a long time that collagen, or more properly the collagen class of proteins, is constructed on some unknown plan of molecular architecture totally different from that of any other protein. This follows from its unique large-angle X-ray diffraction pattern and its characteristic amino acid composition.

I shall return to both of these in more detail later, but first it must be pointed out that in this same year, 1942, two observations were made which, in further development, have had an important influence on our present position with respect to the structure of the collagen fibril. These were the determination of the true axial repeat period of collagen fibrils as about 640 A (1), and the direct visualization of this period in the electron microscope (2).

At the time of this pioneer work on the electron microscopy of collagen, the technique had not yet achieved the great resolution attainable today, and the period appeared only as a pair of alternating light and dark bands. Over the intervening years, finer and finer details of a complex intraperiod band pattern have been revealed, until today under the proper conditions as many as 13 bands, some of which are only 15 A in width, can be discerned within the repeating period (3).

What is the significance of this banded structure? Later on it will be shown how much the study of the spatial relations of this pattern and those exhibited by other structural forms of collagen has contributed to our understanding

LIFE LINES

Dr. John H. Highberger received his B.S. degree from the University of Pittsburgh in 1923, his M.S. from the University of Cincinnati in 1924, and his Ph.D. in bacteriology from the latter institution in 1926.

After serving on the staff of the University of Cincinnati from 1923 to 1945 and as head of the Leather Technology Department of General Dyestuff Corp. from 1945 to 1948, Dr. Highberger joined the United Shoe Machinery Corp. where he has been Associate Director of Research since 1952.

A member of many learned and professional societies, he has been a recipient of the Moffat Medal awarded by the Foundation of the Tanners' Council and both Vice-President (1940-42) and President (1942-44) of ALCA.

Dr. Highberger has been the author of many papers on such topics as the chemical mechanism of tanning, the chemistry of skin proteins, and collagen fiber structure.

of the internal architecture of the collagen fibril. At the moment, however, we are interested only in what causes the banded appearance of the fibril when viewed in the electron microscope. In the very early work no special means were used to accentuate the appearance of the bands (except for cleaning procedures designed to remove obscuring debris from the fibril surface), but since the development of the concept of the "electron stain" phosphotungstic acid (PTA) (4) or other polar compounds which combine specifically with the collagen and which contain heavy atoms have been used for this purpose. It is, however, clear that the PTA is not the cause of the bands, but that these arise because of structural features within the collagen itself. The work of Kühn *et al.* (5, 6) has shown that certain spatial arrangements of the collagen polar groups (the guanidino groups of arginine, in the case of PTA) are necessary for the fixation of the "stain." This observation, together with the fact that gelatin does not show a banded structure, permits the conclusion that the latter arises only when the polypeptide chains of the collagen are packed together in a definite, orderly manner, and moreover, only when the chains maintain their native helical configuration. The nature of this configuration will be discussed below.

Bear (7) had earlier interpreted certain features of the small-angle X-ray diffraction pattern to indicate that the collagen fibril contains alternating regions of higher and of lesser order. He advanced the theory that the regions of higher order consisted predominantly of amino acid residues having smaller than average side chains, such as the relatively nonpolar or weakly polar glycine, alanine, proline, and hydroxyproline. The regions of lesser order, on the other hand, were assumed to be rich in strongly polar residues such as arginine, lysine, and aspartic and glutamic acids. The bulkier-than-average side chains of these residues would tend to make the packing of the polypeptide chains in these regions less compact and of a lower degree of order. Through a study of the effects of PTA on the small-angle X-ray pattern of collagen, Bear *et al.* (8) were able to identify the regions of lesser order, into which the PTA selectively penetrates, with the dark, electron-dense bands seen in the electron micrographs. Similarly the light interbands were identified with the regions of higher order, and the fact that the PTA treatment had little if any effect on the large-angle X-ray pattern was shown to be compatible with the view (9) that this diffraction pattern arises from the interband regions.

According to this view, the polypeptide chains of collagen should contain regions that are rich in strongly polar amino acid residues and very poor or lacking in nonpolar residues, and other regions in which the reverse is true. Since many of the bands and interbands are only 15 A in width, these regions could extend over relatively few amino acid residues. The work of Grassmann *et al.* (10) on peptides isolated from tryptic digests of collagen has shown that this situation does exist. These workers determined the amino

acid compositions of a number of peptides isolated in this way and shown to be homogeneous chemical entities by rigid criteria. If these peptides were listed in the order of increasing polarity, that is, in the order of increasing content of diamino and dicarboxylic acids (expressed as mole per cent), the order was also that of decreasing content of proline plus hydroxyproline. Glycine was present in all peptides, and nearly always in the amount of one-third of the total residues. An especially interesting peptide is the one designated S_f. This has the following structure (the exact sequences of the residues enclosed in parenthesis and brackets have not been determined):

H_2N-gly-ser-ala-(thr, leu, gly)-[10 pro, 5 hypro, 12 gly, 2 ala, ser, 2 tyr, glu] - phe-glu-leu-asp-asp-COOH

Note that this peptide has a relatively nonpolar end and a strongly polar end (the C-terminal end, which contains within the sequence of the last five residues all of the strongly polar residues except one). If it is assumed that the remaining glutamic acid residue and the two tyrosine residues are actually a part of the C-terminal section, then the middle part (within the brackets) is composed mostly of glycine, proline, and hydroxyproline, plus two alanine and one serine residues. In other words, a section of the chain extending for thirty residues is composed exclusively of small nonpolar or weakly polar amino acid residues. It seems probable that this part of the peptide contains sequences of the type

-gly-pro-hypro-

postulated by Schroeder *et al.* (11) and actually isolated by Kroner *et al.* (12).

Tomlin and Ericson (13) have recently shown that the feature of the small-angle X-ray pattern (the "fanning" of the layer lines), which Bear had interpreted as showing the presence of regions of two degrees of order, can equally well be interpreted as showing the presence of longitudinal shear in the fibril, and they have given reasons for believing that the latter is the correct interpretation. It is to be noted that the essentials of the above theory of the origin of the bands are the presence of regions rich in strongly polar residues, supported by the chemical evidence just discussed, the steric relations of these groups, and the presence of the native helical configuration of the polypeptide chains. The existence of regions of higher and lower order, while an essential of the original theory of Bear, is not requisite to the theory as modified by Kühn.

The structure, proposed by Rich and Crick (14), which is now generally accepted as accounting for the large-angle pattern may best be understood by considering Fig. 1. The polypeptide chain configuration is that of Polyglycine II, previously worked out by Crick and Rich (15), two chains from which are shown schematically at (*a*) in Fig. 1. These are helical coils arranged to have three-fold left-handed screw axes with a translation along the

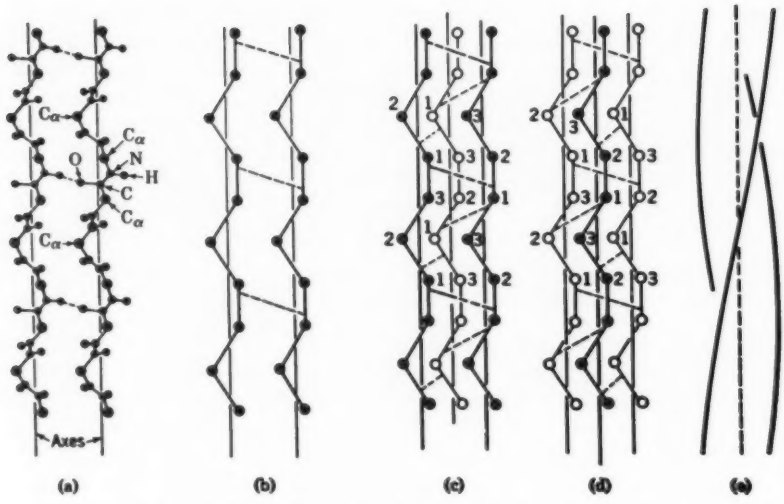

FIGURE 1.—Schematic illustration of the derivation of the collagen structure from the Polyglycine II lattice. From A. Eich and F. H. C. Crick (14).

axis of about 3 A, representing one amino acid residue. The collagen structure is formed of a group of three chains having this configuration and held together by hydrogen bonds formed between the carbonyl and imino groups of different chains. The Polyglycine II structure consists of a hexagonal close packing of the individual chains shown in (*a*), and it is found that there are two ways of taking a group of three chains from this structure. The remainder of Fig. 1 shows the conversion of the basic polyglycine structure to the collagen structure in each of these ways, giving rise to two alternative structures that are very similar.

In (*b*) of Fig. 1 the same two chains are shown as in (*a*), but here, in order to reduce the complexity of the remaining diagrams, only the α-carbon atoms are shown. The hydrogen bonds between the CO and NH groups are shown as dotted lines. In (*c*) a third exactly similar chain has been added *behind* the preceding two. This gives the basic structure designated Collagen I. In (*d*) the third chain has been added *in front* of the original two. This gives the basic structure designated Collagen II. The actual collagen structure is formed by subjecting the group of three chains to a twisting deformation such that the chains coil around each other in a gradual right-hand helix. This coiled-coil structure is shown diagrammatically at (*e*) in Fig. 1.

In (*c*) and (*d*), the three different kinds of sites which arise because of the three-fold symmetry of the screw axis are numbered 1, 2, and 3. In Poly-

glycine II all these sites are of course occupied by glycine, but in collagen glycine makes up only one-third of the total residues. This composition suggests that every third residue is glycine, and this is strongly supported by the work of Grassmann *et al.* (10) on collagen peptides, already mentioned, as well as by that of others. In both Collagen I and Collagen II site 1 must be occupied by glycine because this site is always close to the center of the group of three chains, and there is not enough space to accommodate the side chains of the other amino acid residues. The other two sites can be occupied by any residues. One of the unique features of this structure is that sites 2 and 3 can both be occupied by proline or hydroxyproline. These, however, fit more readily into structure II, a slight deformation being required in structure I. Since the sequence glycine-proline-hydroxyproline has been shown (12) to account for a significant portion of the total proline and hydroxyproline, the structure must be able to accommodate it. In this case, in both structures, site 2 would be occupied by proline and site 3 by hydroxyproline.

A significant difference now becomes apparent between structures I and II. Gustavson (16) has advanced the theory that the hydrothermal stability of collagen fibers in the range 40°–65 °C. is dependent significantly upon interchain hydrogen bonding between the hydroxyl groups of hydroxyproline and peptide carbonyl groups on neighboring chains, and he has adduced evidence in support of this concept, showing that the shrinkage temperatures of various types of collagen are directly proportional to their hydroxyproline contents. If this type of bonding does indeed occur, as seems probable, in the case of structure I it will be intramolecular, within the group of three chains, since site 3 lies close to the center of the group. In the case of structure II, however, site 3 lies away from the center, and here this type of hydrogen bonding must be between groups of three chains, that is, intermolecular. Doty and Nishihara (17) found that the denaturation temperature of three soluble collagens is proportional to the hydroxyproline content, with a constant difference from the thermal shrinkage temperature, and they believe that this supports the Collagen I structure, as showing that the hydroxyproline bonding is intramolecular. Witnauer and Fee (20) later pointed out that the difference between the denaturation temperature and the shrinkage temperature is actually much smaller than stated by Doty and Nishihara, whose value of about 27 °C. was largely the result of measuring the two quantities under different conditions. This of course does not affect the conclusion about the hydroxyproline bonding.

On the other hand, some doubt is thrown upon the hydroxyproline bonding theory by the work of Watson and Sylvester (18), who failed to find any correlation between shrinkage temperature and hydroxyproline content in a group of invertebrate collagens. Piez and Gross (19) also have found that the shrinkage temperature in a group of vertebrate collagens is more exactly

related to the total imino acid content (the sum of proline and hydroxyproline) rather than to the content of hydroxyproline alone. They have interpreted this as indicating that the molecular structure of collagen is maintained in large part by restrictions on changes in polypeptide chain configuration imposed by the pyrrolidine rings of proline and hydroxyproline, particularly where these are present as adjacent residues, rather than by hydrogen bonding through the hydroxyl group of hydroxyproline. It was pointed out by these authors that the observation of Doty and Nishihara can also be explained in terms of the Collagen II structure, if the total imino acid content is also proportional to the denaturation temperature, and if the hydroxyproline hydroxyl does not play a unique role. That the latter may be the case is suggested by the existence of data indicating that a decrease in the number of hydroxyproline hydroxyl groups is compensated for by an increase in serine and threonine (Eastoe and Leach [21]).

Burge and Hynes (22) had also found that the thermal denaturation temperature in solution of five vertebrate collagens correlated more closely with the total pyrrolidine residues than with the hydroxyproline content. They came to essentially the same conclusions as Piez and Gross regarding the importance of these residues in the stability of the structure.

It is therefore apparent that at the present time it is impossible to decide definitely between structures I and II. Consideration of all the evidence, however, leads to the conclusion that structure II is probably the correct one, and it is generally agreed that it is more satisfactory on purely crystallographic grounds.

In Fig. 2 is shown a photograph of a model of the Collagen II structure, due to Rich. A feature of interest is a helical groove which winds along the assemblage of chains, a feature which arises because at the sites occupied by glycine close to the center of the group of chains, there are no side chains, but only hydrogen atoms. The helical ridge on either side of the groove consists of the side chains of the residues occupying the other two sites of the triple residue sequence. In the case shown, these are all pyrrolidine rings, since the portion of the structure shown is composed of the sequence glycine-proline-hydroxyproline. On the basis of the considerations discussed above, the model shown in Fig. 2 comprises a part of the structure at the interband regions of the fibril. In other portions of the structure, at the band regions, the helical ridge will be occupied by other and bulkier side chains, many of which bear strongly polar groups which are involved in the lateral bonding of the fibrillar structure.

Early in the study of the structure of the collagen fibril the term "protofibril" was coined (Schmitt, Hall, and Jakus [2]) to connote the smallest columnar array capable of carrying the characteristics of collagen, and the lateral aggregation of which produced the collagen fibril visible in the electron microscope. For many years thereafter, it was not known whether the proto-

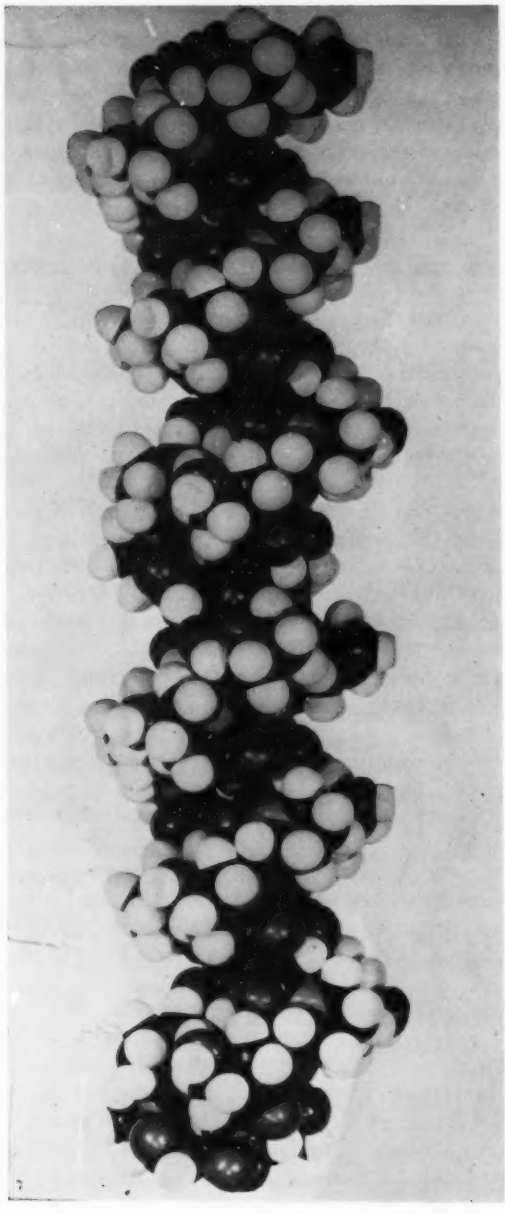

FIGURE 2.—Van der Waals model of Collagen II, containing the repeating sequence -glypro-hypro-. Courtesy of A. Rich.

fibril consists of a single polypeptide chain, or whether more than one chain is involved in its structure. It is now clear that the protofibril consists of an indefinitely long strand composed of three polypeptide chains in the helical configuration just described. The fibrillar structure is produced by the lateral association of these protofibrillar units, probably in hexagonal packing, and bonded by the interaction of the polar groups in the band regions of adjacent protofibrils into a precisely ordered array having an axial repeating period of about 700 A.

THE TROPOCOLLAGEN MACROMOLECULE AND ITS AGGREGATION STATES

Consideration of the fibrillar structure just described naturally gives rise to the question: Is there such an entity as a collagen molecule, and if so, what is its relation to the protofibril? The answers to these questions have been arrived at by a detailed study in the electron microscope of several atypical forms of collagen produced from solutions of soluble collagens, as well as by the application of the methods of physical chemistry to such solutions.

Work on the soluble collagens was stimulated by the observation of their widespread occurrence made by Orekhovich *et al.* (23) in 1948. During the next few years it was found possible to produce reversibly from such solutions, in addition to the native fibril exhibiting the familiar 700 A period, a number of new and quite different forms. For a summary of this work, see Schmitt, Gross, and Highberger (24) and Highberger (25). The usual method of reconstituting collagen fibrils from solution is to dialyze under such conditions that the pH and ionic strength at equilibrium fall within certain limits. Early in the study of such fibrous precipitates with the electron microscope the presence of a new fibrous form having a period several times that of the native fibril was observed (26). Later it was found possible to produce this form, which was called fibrous long-spacing (FLS), reversibly from any collagen solution by the addition of α-1 acid glycoprotein before dialysis (27). A second, very important segmental form was discovered when neutral salt extracts of connective tissue were dialyzed against an acid buffer, and it was found that this form, called segment long-spacing, could be precipitated reversibly from any acid solution of collagen by the addition of adenosine triphosphoric acid (ATP) (28).

These facts strongly suggested the existence in collagen solutions of a unit particle which produces the various forms observed by aggregating in different ways (28). This unit particle was given the name "tropocollagen" (29), meaning a substance capable of turning into collagen, in order to differentiate it clearly from the meanings already attached to such terms as "precollagen" or "procollagen." Study of the band patterns of the native, FLS, and SLS forms suggested that the tropocollagen (TC) particle is a thin

rod about 2800 A (the length of the SLS and FLS period) long, and possessing a polarized or asymmetric arrangement of amino acid residues in its constituent polypeptide chains. The various observed forms are then produced by packing these particles in the arrangements illustrated diagrammatically in Fig. 3, in which the polarized nature of the TC particle is indicated by repre-

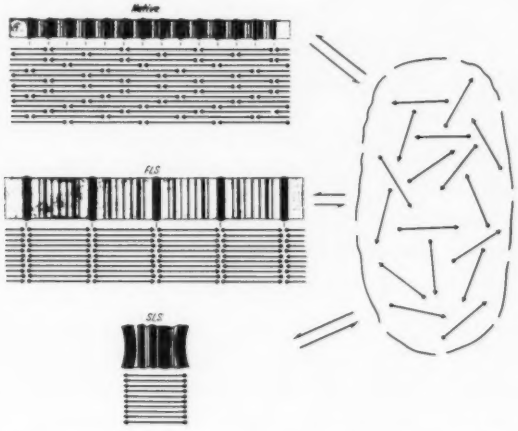

FIGURE 3.—Schematic representation of the modes of aggregation of the TC macromolecules in three structural forms, as produced reversibly from an acid solution of TC.

senting it as an arrow. It is to be noted that according to this scheme the native-type fibril is formed by a staggered packing in which the TC units all point the same way, the FLS form is composed of an antiparallel arrangement with the ends of the TC particle approximately in register, and the SLS form consists of a parallel packing with the ends in register. The polarized, symmetrical, and polarized natures of the respective band patterns are thus explained by these arrangements of a fundamentally polarized unit particle (24).

It is evident that two types of aggregation of the TC particles, linear and lateral, are variously involved in the production of these forms. Linear aggregation of the head-to-tail type forms the protofibril previously discussed. Under physiological conditions of pH and ionic strength these protofibrils interact laterally to form the native-type fibril. This lateral aggregation is the result of an orderly interaction between sets of polar groups on adjacent protofibrils, giving rise to the band pattern characteristic of the native-type fibril. How, then, does it happen that protofibrils are also able to interact laterally in a different way, under essentially the same conditions, to form FLS? The answer is, obviously, that α-1 acid glycoprotein

has combined with some of the polar groups of the protofibril, altering its charge profile, and resulting in an entirely different pattern of laterally interacting groups. Similarly, combination of ATP with the TC particle—probably primarily with its lysine ε-amino groups—greatly lessens the end-to-end attraction of the particles and results in the precipitation of the SLS form in which the lateral interaction occurs with the ends in register.

At the time the tropocollagen hypothesis was first stated, it was not certain whether this particle is the molecular unit of collagen or whether it represents an aggregate of such units which for some reason participates in the observed reactions as a single kinetic unit (24). Because of the evidence from electron microscopy and X-ray diffraction of a fundamental repeating period of 700 A in the collagen fibrillar structure, the idea that the molecular unit must have this dimension was well established. Work to be described in the following, however, has left no doubt that the TC particle, four times the collagen period in length, is in fact the molecular unit of the collagen structure. For this reason it is now referred to as the TC macromolecule. The prefix macro- is used because the TC particle, being an aggregate of hydrogen-bonded polypeptide chains, according to the Rich-Crick structure, does not meet the definition of a molecule in the strict physicochemical sense. (This is to be regarded as applying primarily to the collagen predominantly present in the usual acid soutions and does not mean that collagen molecules in the strict sense may not exist. See below.)

Confirmation of the existence in collagen solutions of a particle having the dimensions postulated for TC soon appeared in the work of Boedtker and Doty (30). These workers studied collagen solutions by various physical methods, including ultracentrifugation, light scattering, viscometry, osmometry, and flow birefringence. The results of several previous investigators, obtained principally by light scattering, had indicated molecular weights of several millions for the components of such solutions. Boedtker and Doty (30), however, were able to show that such solutions were heterodisperse, containing small amounts of highly polymerized material of high molecular weight. When such material was removed by high-speed centrifugation at relatively low protein concentration, it was possible to prepare monodisperse solutions of a particle of molecular weight 345,000 and having dimensions of 14 by 3000 A. This particle was obviously identical with the hypothesized TC.

With an improved electron microscope technique Hall and Doty (31) were able to resolve the TC macromolecules and measure their dimensions directly (see Fig. 4). Using the same solutions on which the physical measurements had been made, they obtained a weight-average length of 2820 A, only 6% less than the value found by Boedtker and Doty. Furthermore, these same solutions, when reconstituted into the FLS form, gave structures with a period averaging 2700 A, in good agreement with the particle length.

FIGURE 4.—TC macromolecules from an acetic acid solution of ichthyocol; shadow cost with platinum on a cleaved mica substrate. × 100,000. Courtesy of C. E. Hall.

The above results were all obtained on ichthyocol, the collagen of the carp swim bladder tunic. Later, Doty and Nishihara (17) carried out similar physical studies on solutions of calfskin collagen and found macromolecular properties very similar to those of ichthyocol, although the macromolecule appeared to be slightly larger, having a diameter of 13.5 A, a length of 3300 A, and a molecular weight of 360,000. Later measurements by Hodge and Schmitt (32) on long-spacing forms reconstituted from calfskin collagen solutions showed very sharp distributions around 2800 A for the period lengths. In accordance with this and with other evidence to be discussed below, it is now believed that the length of the TC macromolecule is exactly four times the length of the axial period of the native fibril.

THERMAL DENATURATION OF THE TROPOCOLLAGEN MACROMOLECULE

The fact that collagen undergoes a conversion to gelatin on heating in water is probably the oldest piece of information we possess about this material. Under these conditions, the TC macromolecule dissociates to what is called "parent gelatin" at its denaturation temperature. The process is characterized by sharp drops in viscosity and optical rotation. In 1955

Orekhovich and Shpikiter (34) studied this reaction in the ultracentrifuge, in the case of the acid-soluble collagen (called by them "pro-collagen") of rat skin. They found that two components were produced in the denaturation and that these were of unequal weights. In a later investigation (35) they introduced the now generally accepted terminology in which the lighter component is called α and the heavier β. In further work (36) a process was developed by means of which the two components were separated by fractional precipitation from urea solution with ammonium sulfate. They found the two to occur in a 1:1 weight ratio, and concluded that the macromolecule contains two molecules of the α- and one of the β-component.

Boedtker and Doty (30) in their original work on ichthyocol had also studied the thermal denaturation and had interpreted their light-scattering results to indicate that the macromolecule dissociated into three components, which they identified with the three polypeptide chains of the Rich-Crick structure. Later, however, Chun and Doty (33) reinvestigated the ichthyocol denaturation by ultracentrifugation and found that actually only two components are formed. They found these to have molecular weights of about 80,000 and 160,000 respectively.

Similarly, in the thermal denaturation of acid-soluble calfskin collagen, Doty and Nishihara (17) found again that only two components are formed, of molecular weight about 120,000 and 230,000. A similar observation was also made on cod skin collagen, so that the dissociation into two components on thermal denaturation began to appear to be characteristic of all collagens.

How are the two components to be explained in terms of the three-chain Rich-Crick structure? One way was suggested by Orekhovich and Shpikiter (36) who interpreted the molecular weights and weight ratio found by them in rat skin collagen to indicate the occurrence of two molecules of α- and one of β-component in the macromolecule. The values found by Doty and Nishihara (17) in the case of calfskin collagen, however, do not permit this interpretation, and these authors believe this macromolecule to contain one molecule each of the α- and β-components. In order to form the three-chain structure, it would then be necessary for the β-component to fold back on itself. This concept was further strengthened by the observation (17) that the β-component, on raising the pH of its solution to 12, gives rise to material which is comparable in the ultracentrifuge to the α-component. The possibility is thus suggested that the β-component may consist of two units, similar in size to the α-component, and held together by an alkali-sensitive bond to form two of the chains of the three-chain structure.

A method which permits the fractionation of thermally denatured collagen in gram amounts has been developed in our laboratory (37). The method is based upon gradient elution chromatography on a carboxymethyl cellulose column operated at pH 5.0. A typical chromatogram of calfskin acid-soluble collagen is shown in Fig. 5. The α- and β-components are well resolved by

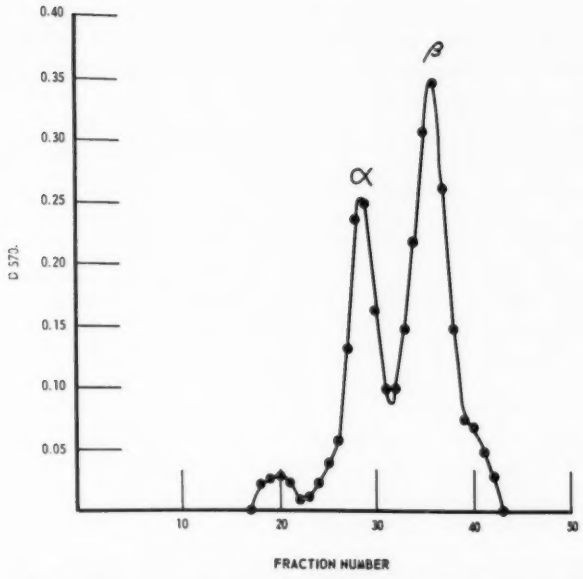

FIGURE 5.—Effluent diagram of thermally denatured calfskin collagen on carboxymethyl cellulose column at pH 5 and 45°C. The nature of the small forepeak, representing 2–3% of the total material, is unknown.

this method, and a detailed study of each is in progress. Amino acid analyses of the separate components have been carried out, and the results are in general agreement with those of Piez, Weiss, and Lewis (38). The two components are very similar in amino acid composition, but definite differences do exist. The contents of histidine, valine, leucine, isoleucine, and hydroxylysine are significantly higher in the β- than in the α-component, while lysine is higher in the α-component. Proline and hydroxyproline also appear to be slightly higher in α.

Our results, however, differ from those of Piez, Weiss, and Lewis with respect to the relative proportions of α and β present. We have consistently found, by nitrogen analysis, a weight ratio of α:β of 1:2, in agreement with Doty and Nishihara (17), while Piez, Weiss, and Lewis derive a 1:1 ratio by calculation from their amino acid results. The source of this discrepancy is not known at present. We have also confirmed the observation of Doty and Nishihara that the β-component contains an alkali-sensitive bond.

Kessler, Rosen, and Levenson (39) have also fractionated rat tail tendon collagen by gradient elution chromatography on carboxymethyl cellulose. Their results indicated at least four fractions, the relative proportions of which

depended upon the acetic acid concentration of the collagen solution. The significance of this is not clear at present, although it seems probable that it might reflect further degradation of the major components under the conditions of these experiments.

ORIGIN OF THE NATIVE-TYPE BAND PATTERN

The statement has frequently been made since the original discovery of the banded appearance of native collagen fibrils in the electron microscope that this is the "fingerprint" of collagen. In the sense of a characteristic which permits instant recognition, the statement is undoubtedly true, but since the recognition of the modes of aggregation of the TC macromolecule in the native fibril and in SLS, it has become apparent that the band pattern of the latter form is the true "molecular fingerprint." This is because only in the latter are the TC macromolecules lined up in a parallel manner with ends in register, so that the fluctuation in density along the "stained" structure accurately represents the distribution of polar groups along the length of the macromolecule. In the native form, the band pattern is the resultant of the staggered mode of aggregation, each band resulting from contributions from several loci along the TC macromolecule.

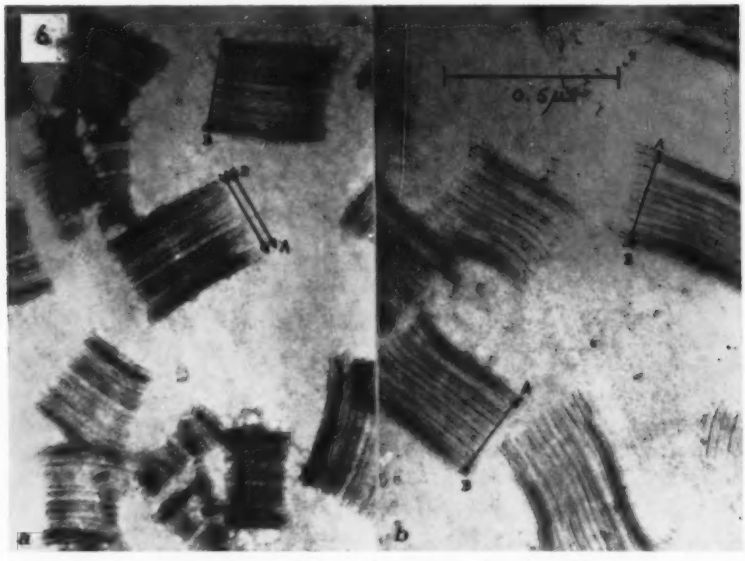

FIGURE 6.—Monomeric SLS precipitated from an aged acetic acid solution of calfskin collagen with ATP. (*a*) Stained with PTA (*b*) Stained with cationic uranium. × 60,000. The orientation of the TC macromolecules is indicated by the arrows labeled *A* and *B*. From Hodge and Schmitt (32).

As has already been explained, the "electron stain" customarily used to bring out the band patterns of these structures is phosphotungstic acid (PTA). This, being an anionic stain, combines with the basic groups which are sterically situated in such a manner as to be able to bind the large electron-dense phosphotungstate ion (5, 6). It follows that the band pattern obtained by PTA staining of SLS represents a "map" of the loci, along the TC macromolecule, of the basic groups fulfilling the above requirements. In a similar manner, a stain consisting of an electron-dense cation should reveal the loci of acidic groups. Such a substance is found in uranyl nitrate, and Hodge and Schmitt (32) were able to prepare cationically stained SLS by using this material. Figure 6b shows the result obtained, while Fig. 6a is the same SLS preparation stained with PTA. The marked difference between the two band patterns is obvious. When a detailed comparison of the two is made, however, by aligning them side-by-side with the ends in register (Fig. 7), it becomes apparent that the positions of the bands correspond quite closely in the two cases and that the major difference is in the band intensities. The fact that in practically all cases bands in one pattern have counterparts in the other indicates that both basic and acidic groups occur in quite localized

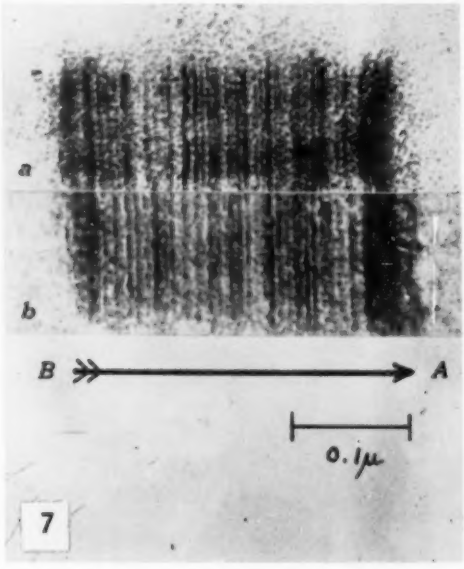

FIGURE 7.—Two individual segments from the same preparation as in Fig. 6. (*a*) Stained with cationic uranium. (*b*) Stained with PTA, showing the close correspondence in band positions and the considerable differences in intensities. The arrow labeled *A* and *B* indicates the molecular orientation. × 200,000. From Hodge and Schmitt (32).

regions all along the length of the macromolecule. In some cases, however, one or the other type predominates, while in others there is an approximately equal distribution.

These band patterns, whether anionically or cationically stained, emphasize the polarized nature of the TC macromolecule. As will be seen later on, it is important to be able to distinguish one end from the other in these and related structures. Hodge and Schmitt (44) for this reason adopted the convention of labelling as *A* the end closest to the conspicuous interband which occurs at about 55% of the length of the SLS structure in PTA-stained specimens. A similar conspicuous interband occurs much closer to the *A* end in cationically stained preparations (see Figs. 6 and 7).

It is an interesting fact, from the standpoint of tanning chemistry, that the cationic chrome solutions used in tanning react with collagen in essentially the same way as uranyl nitrate. Because of the much lower electron density contributed by the chromium, however, it is not as good an "electron stain," although specimens stained in this way have been used in the electron microscope study of chrome tanning (40).

At the time of the recognition of the general modes of aggregation of the TC macromolecule in the various forms (28), the exact nature of the staggered aggregation in the native fibril was not known. As it became evident that the TC macromolecule is four times the length of the native period, it appeared that the staggered arrangement must be such that each macromolecule is displaced relative to its neighbor by one-quarter of its length. If this hypothesis is correct, it should be possible to synthesize the native-type band pattern from that of SLS by summing up the individual contributions to density from each band brought into coincidence by the quarter-stagger packing arrangement. Hodge and Schmitt (32) accomplished this by a photographic method in which the image of a single PTA-stained SLS was printed by multiple exposure with a longitudinal displacement between successive exposures of one-quarter of the SLS length. The result is shown in Fig. 8 at *b*, *a* being the original single SLS, and *c* a PTA-stained native fibril. It is seen that there is a close correspondence, both in band position and intensity, between the resultant of the multiple exposure and the native-type band pattern.

Kühn (6) has accomplished a similar synthesis of the native-type band pattern from that of SLS, using the alternative method of summing up the photometer curve of the latter with a displacement of one-quarter the length of the SLS.

While the above results offer convincing evidence of the correctness of the quarter-stagger theory of the native-type fibrillar structure, Hodge and Schmitt (32) were also able to adduce a more direct proof in another way. It was found that when reconstituted native-type fibrils were exposed to a solution of TC macromolecules containing ATP, at a pH value favoring the

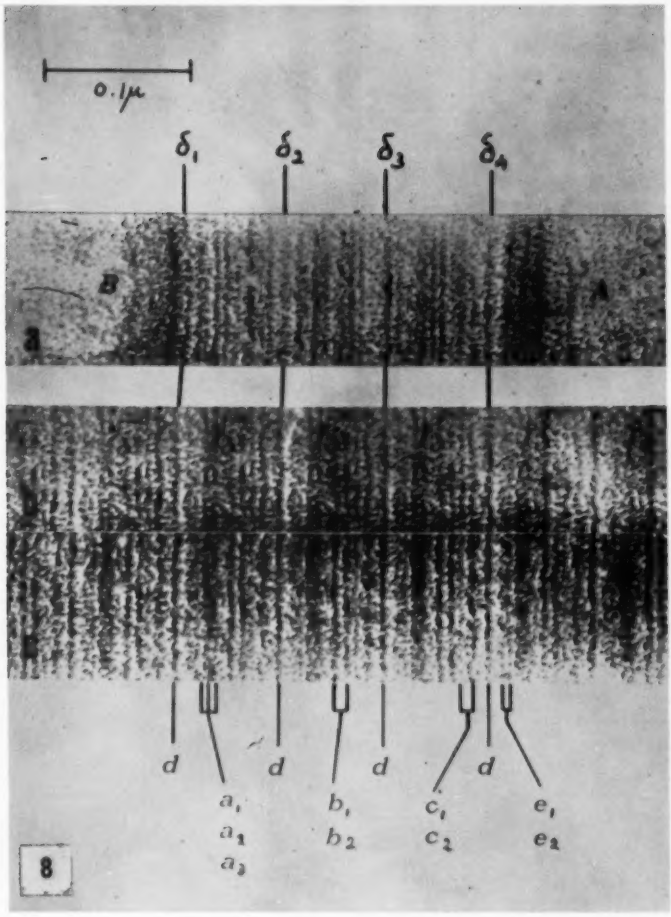

FIGURE 8.—Composite electron micrograph illustrating the "optical synthesis" of the native-type band pattern from that of SLS. (*a*) Image of a single segment of monomeric SLS, stained with PTA. (*b*) Pattern produced by multiple printing of image (*a*), with longitudinal displacement between successive exposures of one-quarter the length of the segment in (*a*). (*c*) Band pattern of native-type fibril stained with PTA. Note that the positions and densities of (*b*) and (*c*) correspond closely. × 250,000. From Hodge and Schmitt (32).

formation of SLS, the latter formed as outgrowths from the surfaces of the native-type fibrils, giving rise to the dimorphic forms shown in Figs. 9 and 10. In all cases the SLS forms were oriented in the same direction with

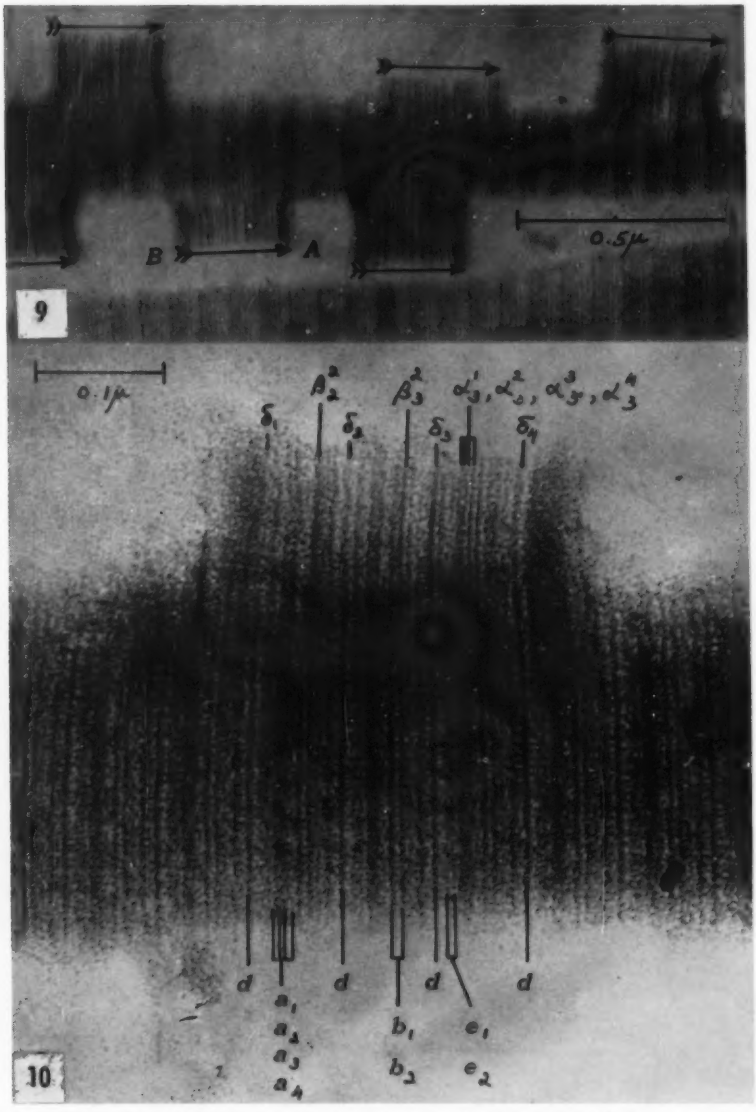

FIGURE 9.—Dimorphic structure produced by exposing native-type fibrils to a solution containing TC macromolecules and ATP at a pH value favoring the formation of SLS-type aggregates. Arrows indicate the orientation of the TC macromolecules. See text for description. Stained with PTA. × 74,000. From Hodge and Schmitt (32).

FIGURE 10.—View at magnification 220,000 of one region from the preparation of Fig. 9, showing that each band in the native-type structure is continuous with one of four "equivalent bands" in the SLS form. See text. From Hodge and Schmitt (32).

respect to the polarity of the native-type fibrils, and each band of the SLS structures appeared as a continuation of a band in the native-type pattern—the latter extending over four periods for each outgrowth of SLS. On careful examination it was found that, within these four periods, each characteristic band of the native-type intraperiod pattern was continuous with four different bands of the SLS pattern which were separated from each other by one-quarter of the SLS length. Every four "equivalent bands" of the SLS structure therefore give rise, by a summation of their densities, to the observed density of the corresponding band of the native-type structure. Each set of four "equivalent bands" in the SLS pattern contains bands of differing density, and this fact immediately rules out any possibility that the true molecular unit might be only one-quarter of the TC macromolecule—a possibility that is excluded, in any case, by other lines of evidence.

A diagrammatic representation of a structure of the dimorphic type is shown in Fig. 11. Here the TC macromolecules are again represented as

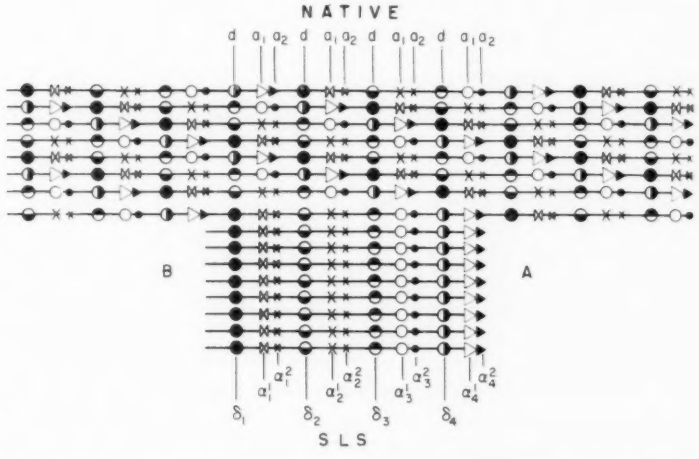

FIGURE 11.—Diagrammatic representation of the packing arrangement of the TC macromolecules in the dimorphic structure of Figs. 9 and 10. To simplify the diagram, only twelve bands are shown (indicated by different symbols) in the SLS form. These produce, by the "hetero-register" resulting from the "quarter-stagger" packing arrangement, three of the bands of the native-type pattern. From Hodge and Schmitt (32).

arrows, with the staining sites along the macromolecular length indicated by various symbols. To avoid complicating the diagram only twelve bands are shown in the SLS structure, these giving rise, as explained above, to three of the intraperiod bands of the native-type structure.

The work summarized above may be taken to have given definitive proof of the TC-staggered aggregation theory of the structure of the native collagen fibril, and to have furnished exact information on the details of the mode of packing of the macromolecules. A further cautionary word must, however, be added. The work described was all carried out on acid-soluble collagen, and the power of the electron microscope as applied to the various forms reconstituted from such solutions has been amply demonstrated. Can we have confidence, however, that the structure so elucidated applies also to those collagen fibers which are not soluble in acid? In view of the identity between the forms with respect to characteristic features observable in the electron microscope, the answer must be that the packing arrangement of the TC macromolecules is identical. There probably, however, are some differences in the intermolecular bonding which give rise to the acid insolubility. It is readily conceivable that during the aging process new stabilizing bonds, probably covalent in nature, are formed. The work of Veis and Cohen (41) has shown the existence of a system of cross-linking bonds in mature collagen, and the presence of an interchain peptide link is strongly suggested by the finding of Mechanic and Levy (42) that a peptide involving the ϵ-amino group of lysine can be isolated from a partial hydrolysate of Achilles tendon collagen. The exact nature of such cross links, and whether they are exclusively intermolecular, or whether some may be intramolecular (giving rise to a true TC molecule), remains to be seen.

THE END-CHAIN HYPOTHESIS

It was pointed out above that the collagen protofibril is formed by the end-to-end interaction of the TC macromolecules. Some light has been shed on the nature of this interaction by an electron microscope study of the effects of sonic irradiation on TC solutions. Nishihara and Doty (43) had previously found that such irradiation produced a drastic decrease in the viscosity of the solution, indicating a fragmentation of the TC macromolecules into shorter pieces. They also found, however, that the optical rotation of the irradiated solution did not decrease but remained nearly at its original value. The only interpretation which could be placed on this is that the helical configuration of the collagen was not destroyed by the sonic irradiation and that therefore the fragments produced must retain their native helical structure. Examination of sonically irradiated TC solutions in the electron microscope by Hodge and Schmitt (44) confirmed this. It was found possible to precipitate with ATP from such solutions fragmentary SLS forms containing recognizable portions of the total SLS band structure (see Fig. 14). The exact nature of the ATP-precipitable material depended upon the time of irradiation, and in agreement with Nishihara and Doty, Hodge and Schmitt showed that the fragmentation is not a random process

but that there is a preferential scission of the TC macromolecules into halves and quarters.

The general results of the electron microscopic investigation of the effects of the sonic irradiation are shown schematically in Fig. 12. In addition to the ATP precipitation, ability to reconstitute native-type fibrils on dialysis

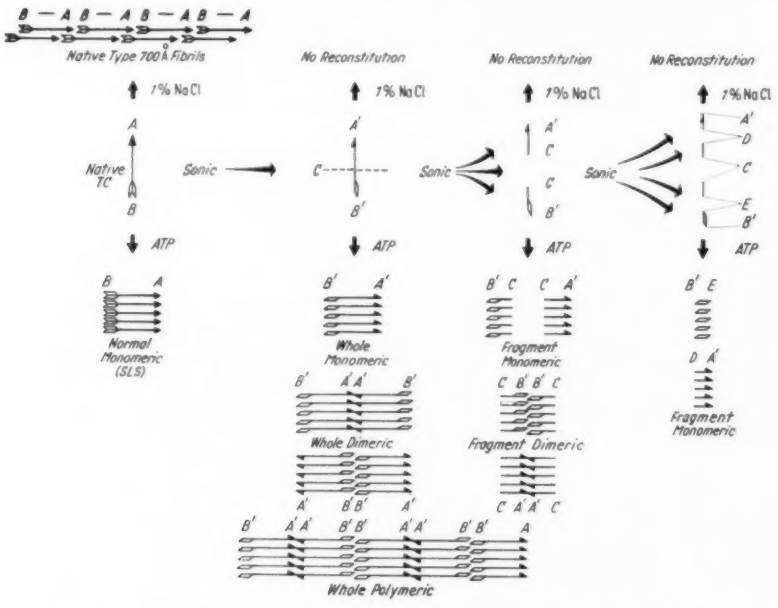

FIGURE 12.—Diagram illustrating the effects of sonic irradiation on the TC macromolecule, as observed in the electron microscope. From Hodge and Schmitt (44).

against 1% NaCl solution was examined in relation to the time of irradiation. The first result noted was a rapid loss of reconstitutability under these conditions. The solutions irradiated for the shorter times, however, which had largely lost the ability to reconstitute native-type fibrils, still gave ATP precipitates of apparently normal SLS. This result strongly suggested that the end regions of the TC macromolecules were most quickly affected by the irradiation, since at this stage the end-to-end interaction capability was inhibited, while the ability to aggregate laterally, without apparent alteration in the length of the resulting SLS, was unaffected. In Fig. 12 this change of unknown nature is indicated by labelling the ends of the affected macromolecules *A′* and *B′*. Other observations, moreover, gave further evidence of some sort of alteration produced in the end regions of the TC macromolecules.

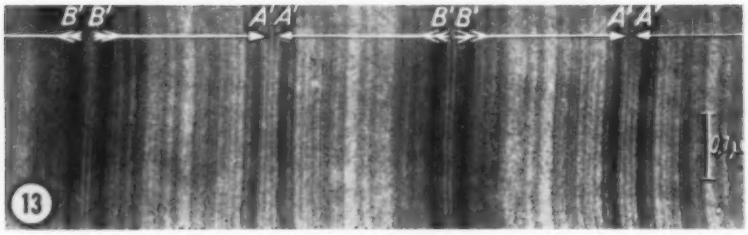

FIGURE 13.—SLS aggregate of whole polymeric type from sonically irradiated calfskin collagen solution, showing linkages of the *A'-A'* and *B'-B'* type. Stained with PTA. × 100,000. From Hodge (45).

The control, unirradiated TC solutions, produced ATP precipitates of SLS which were largely monomeric in form, that is, end-to-end dimers or trimers of the SLS were rarely observed. With increasing time of irradiation, within the time period where reconstitution of native-type fibrils was largely inhibited and before marked fragmentation occurred, two very striking effects were noted. These were an increasing tendency to form polymeric forms of the *A'-A'* and *B'-B'* type, as contrasted with the *A-B* type found in the rare dimers observed in the control, and a very markedly enhanced ability to aggregate laterally. These effects are shown in Figs. 13 and 14.

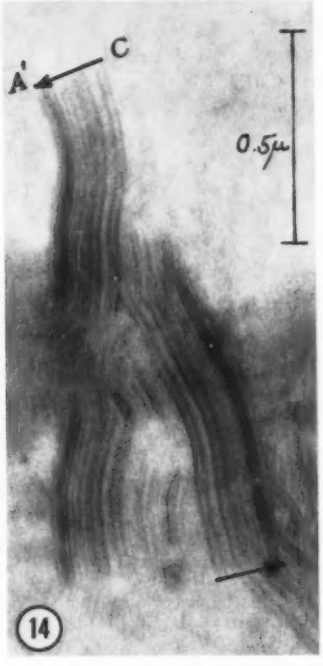

FIGURE 14.—SLS aggregates from sonically irradiated calfskin collagen solutions showing ribbon-like fragment monomeric forms of the type *A'C*. From Hodge and Schmitt (44).

As the time of irradiation was increased, fragmentation of the TC macromolecules occurred, leading first to the formation of fragments of the type *A'C* and *B'C*, by scission of the macromolecule not far from its middle. Finally, these fragments were in turn broken into the pieces *A'D* and *B'E*, representing approximate quarters of the original TC macromolecule (Fig. 12). The formation of these also implies the formation of *DC* and *CE*, but the latter were never observed as ordered SLS type structures. The various SLS-type structures resulting from the sonication were found as monomeric and as polymeric forms, with the following impor-

tant restriction: only those fragments which included *A'* or *B'* ends were observed as polymeric forms. Some of these are shown in Figs. 15 and 16.

In Fig. 16, a direct comparison is made of the band patterns of single SLS (*a* and *c*) with that of a polymeric form produced by sonic irradiation and involving *A'*-*A'* and *B'*-*B'* end-to-end linkages (*b*). It is to be noted that in the *A'*-*A'* linkage the two bands corresponding to the terminal band at the *A* end of the SLS are separated by a distance of approximately 100 A, while in the *B'*-*B'* linkage the two terminal bands of the SLS *B* end are separated by about 180 A. Here, however, a totally new band, indicated by arrow 1 of Fig. 16, has made its appearance between the two terminal bands.

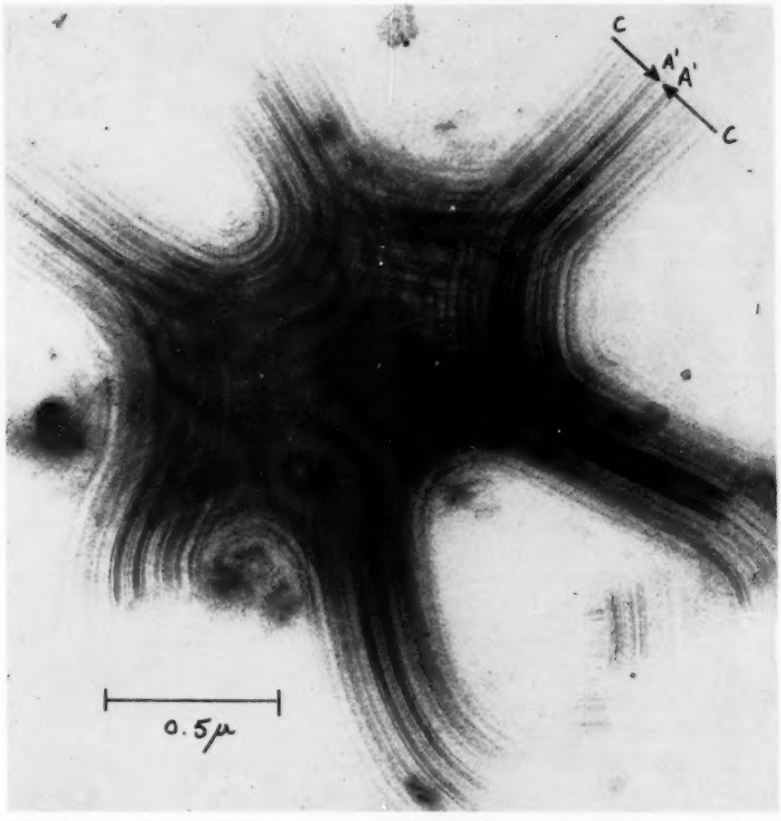

FIGURE 15.—SLS aggregates of the fragment dimeric type *CA'*-*A'C* from sonically irradiated calfskin collagen solution, showing extensive lateral aggregation in the form of "ribbons". PTA-stained. × 55,000. From Hodge and Schmitt (44).

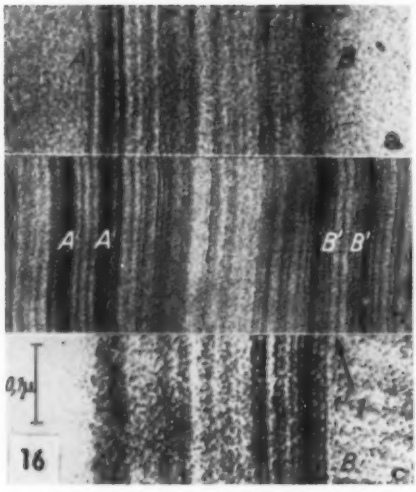

FIGURE 16.—Composite micrograph for comparison of the band patterns of whole monomeric SLS (*a* and *c*) with that of the whole polymeric form (*b*). Two single segments are necessary for the comparison because of the obscuring of portions of the pattern by disorder resulting from the drying of the specimen. The new band observed in the *B'-B'* junction is indicated by arrow 1. Calfskin collagen, PTA-stained. × 120,000. From Hodge and Schmitt (44).

Hodge and Schmitt (44) reasoned as follows on the basis of these observations: If it is accepted that the bands of these structures arise only where the native three-chain helical configuration is maintained, then the suggestion comes strongly to the fore that the *A* and *B* ends of the TC macromolecule possess chain appendages which probably exist in random coil configuration in the monomeric form and which have maximum lengths of about 100 A and 180 A respectively. Boedtker and Doty (30) had previously suggested the presence of such dangling end chains, based on their flow-birefringence and light-scattering data on TC solutions. Hodge and Schmitt (44), however, now suggested that the appearance of a new band in the *B'-B'* junction (Fig. 16) arose from an orderly coiling of the terminal chains about one another to form an ordered helical structure and that this is the mechanism of end-to-end polymerization. The fact that in the sonically irradiated TC solution no polymeric linkages were ever observed other than those involving the original TC ends strongly supports this hypothesis, since it shows that the original ends possess properties which are not found in any of the ends produced by scission.

The chemical nature of the bond is of course unknown, but it may be presumed to involve hydrogen bonding (see below). From the electron micrographs it would appear that the regions occupied by the end chains are probably similar in amino acid composition to the interband regions of the TC macromolecule and therefore are relatively poor in strongly polar groups. It is to be noted that the fact that no new band appears in the *A'-A'* linkage, whereas one does appear in the *B'-B'* linkage, indicates that the *A* end chain differs in amino acid composition from the *B* end chain and is probably poorer in polar groups.

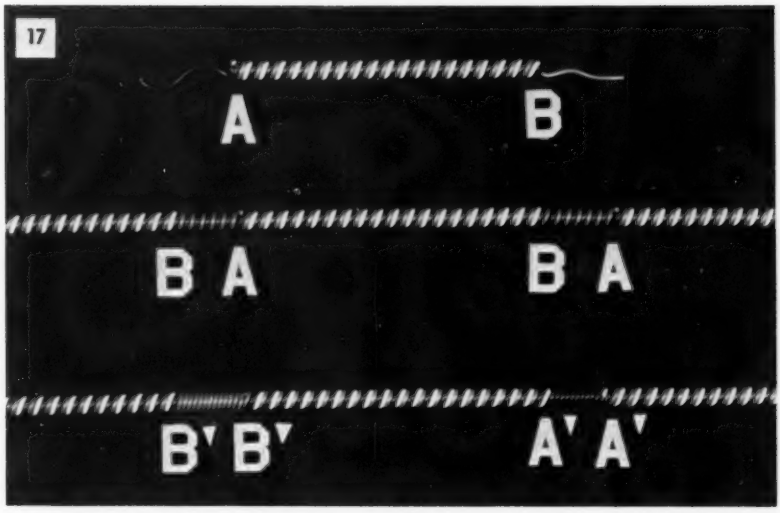

FIGURE 17.—Wire models illustrating the TC macromolecule in solution, and types of end-to-end interaction. See text for description. From Hodge (45).

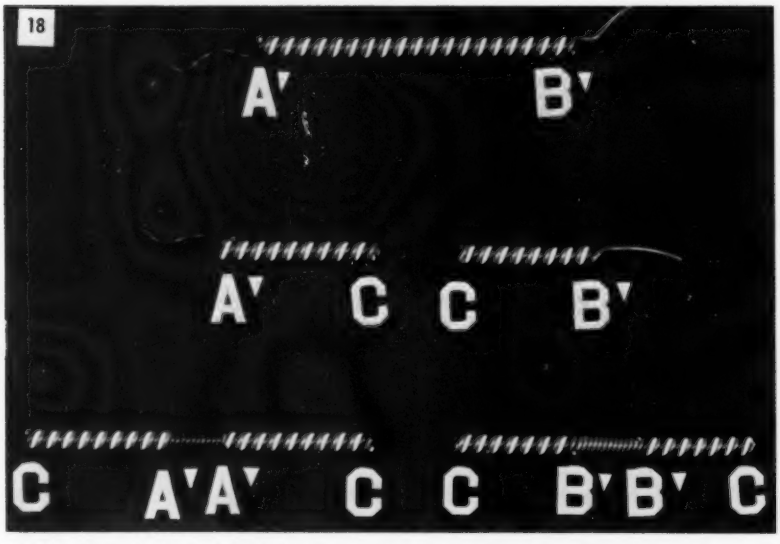

FIGURE 18.—Wire models of the TC macromolecule, illustrating fragmentation by sonic irradiation and the formation of fragment dimeric forms on addition of ATP. From Hodge (45).

Wire models constructed to illustrate the general features of the end chain hypothesis are shown in Fig. 17. At the top is a model of the TC macromolecule in solution, the three-chain helical configuration of the body of the molecule being indicated by coiled wires of three shades. The random-coil end chains are indicated by single wires. In the middle is illustrated end-to-end polymerization of the *A-B* type, leading to the formation of a protofibril, in which the end chains coil about each other to form an ordered junction. At the bottom is shown the formation of the homologous junctions resulting from sonic irradiation. Figure 18 shows the same model, illustrating the effects resulting from sonic irradiation. In the center is shown the initial fragmentation, and at the bottom the mechanism, of the formation of dimeric forms from these fragments.

THE ACTION OF PROTEASES ON THE TROPOCOLLAGEN MACROMOLECULE

It is well known that intact collagen is quite resistant to attack by proteolytic enzymes (the exception being collagenase), requiring denaturation or conversion to gelatin to render it appreciably susceptible. Since this change is from the highly ordered native helical configuration to the random coil of the denatured form, it appeared possible that the end chains of the TC macromolecule, postulated to be in a random-coil configuration in the monomeric form, might be at least partially accessible to enzyme attack. Hodge, Highberger, Deffner, and Schmitt (46) therefore employed this approach in a series of experiments the objective of which was the further characterization of the end chains.

Freshly prepared acid solutions of collagen ordinarily contain, in addition to monomeric TC macromolecules, variable proportions of linear TC polymers. On dialysis of such solutions against 1% NaCl solution native-type fibrils are reconstituted and precipitate from solution. On dialysis against distilled water, so that the pH is gradually raised without increase of ionic strength, linear polymerization occurs without much lateral aggregation, and the solution sets to a water-clear gel. Addition of ATP to this solution during the late stages of dialysis leads to the formation of polymeric SLS-type structures, termed F-SLS (fibrous segment long-spacing). These polymeric forms arise because the SLS crystallizes on the already formed linear polymers. In a similar manner the addition of ATP to an acid solution containing a significant proportion of linear polymers produces a flocculent precipitate of a fibrous character which in the electron microscope is seen to consist of "strings of segments." On the other hand, ATP produces from solutions which have been exposed to proteolytic enzyme action (trypsin, pepsin) only single, monomeric SLS forms, which possess band patterns indistinguishable from those derived from untreated solutions. From solutions acted upon by collagenase, ATP yields no SLS forms at all, as would be

expected. The enzyme-treated TC solutions which produce only monomeric SLS will not reconstitute to form native-type fibrils on dialysis against 1% NaCl solution, nor will they form water-clear gels on dialysis against distilled water. The observed phenomena are illustrated schematically in Fig. 19.

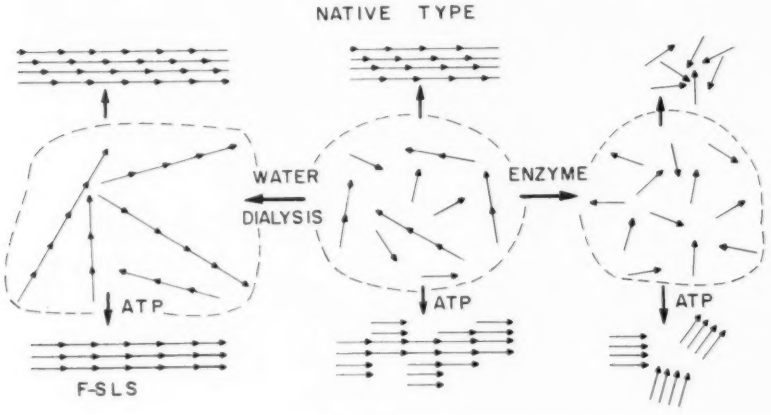

FIGURE 19.—Schematic representation of a typical acid solution of TC containing some linear polymers. Native-type fibrils are formed by dialysis vs. 1% NaCl solution (top center), while the addition of ATP produces a stringy SLS-type precipitate resulting from the growth of individual segments on the pre-existing linear polymers. At left is shown the linear polymerization resulting from dialysis vs. distilled water, leading to the formation of a water-clear gel. The addition of ATP during the late stages of dialysis leads to the formation of polymeric SLS-type structures (F-SLS at bottom left). At right is illustrated the depolymerizing action of proteases such as trypsin. Subsequent dialysis vs. distilled water does not induce end-to-end polymerization (right center and top right), and the addition of ATP produces only single segments, i.e., whole monomeric forms (bottom right). From Hodge, Highberger, Deffner, and Schmitt (46).

These results strongly suggest that the action of proteases (with the exception of collagenase) on the TC solutions results in a depolymerization of the protofibrils without damage to the macromolecular helical structure. Observations on the physicochemical properties of the enzyme-treated solutions gave evidence in support of this interpretation. Calfskin TC solution stabilized at pH 7–8 in 0.5 *M* $CaCl_2$ and tris buffer (47) showed on treatment with crystalline trypsin a rapid but relatively small drop in viscosity, which, however, levelled off at a value consistent with the presence of monomeric TC (see Fig. 20). Similar viscosity decreases have been noted by Gallop, Seifter, and Meilman (47), and by Gross (48). Treatment of the TC solution with pepsin at pH 3.5 also produces similar effects. In all these enzymatic treatments no change could be detected in the optical rotations of the

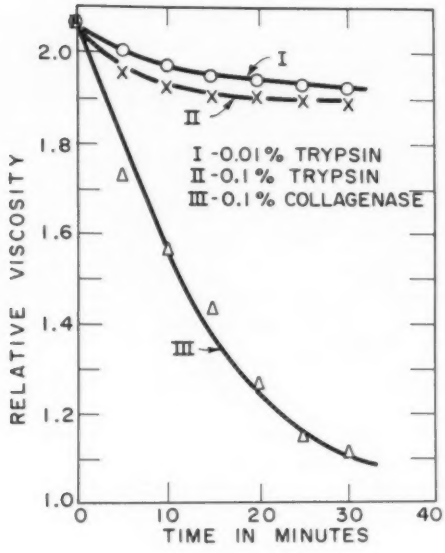

FIGURE 20.—The effects of two proteolytic enzymes (crystalline trypsin and collagenase) on the viscosity of a solution of calfskin collagen. From Hodge, Highberger, Deffner, and Schmitt (46).

solutions, whereas collagenase produces rapid decreases in both viscosity and optical rotation. On following the course of the tryptic action in a pH-stat, it was found that a rapid breaking of a small number of bonds occurs, with the curve soon leveling off at a low value of about twelve bonds per mole of collagen (on the assumption of a molecular weight of 360,000).

All of these results are consistent with the interpretation that the enzyme action results in a depolymerization of the protofibrils without appreciable damage to the helical configuration of the body of the TC macromolecules. The fact that the abilities to reconstitute native-type fibrils and to form water-clear gels are inhibited, however, indicates that the action goes beyond a simple depolymerization and that the end regions of the TC macromolecules are altered in such a way as to inhibit the end-to-end interaction. This is also indicated by the type of SLS structures precipitated by ATP from a TC solution treated with pepsin after exposure to sonic irradiation. Such a solution in the absence of pepsin treatment normally gave with ATP whole polymeric and fragment dimeric type SLS-type structures (see Fig. 13 and 15). After the pepsin treatment, however, it yielded only whole and fragment monomeric SLS forms (Fig. 21).

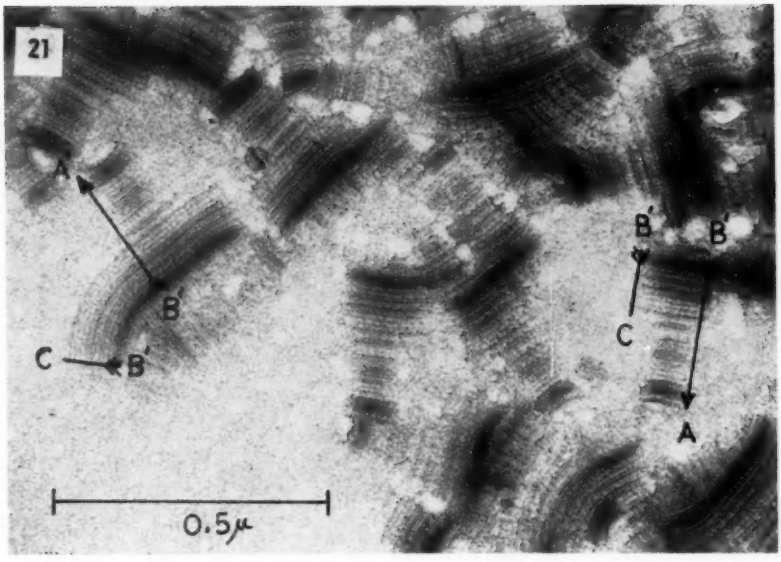

FIGURE 21.—Electron micrograph of a preparation of SLS-type aggregates produced by addition of ATP to a solution of sonically irradiated collagen following incubation with pepsin. Only whole and fragment monomeric forms are observed, while in the absence of the enzyme treatment whole and fragment polymeric forms are characteristically produced. PTA-stained. × 90,000.

It seems very probable that the alteration of the end regions produced by the enzymatic action consists of the splitting off of a peptide or peptides from the postulated end chains. Hodge, Highberger, Deffner, and Schmitt (46) therefore directed their efforts toward the isolation and characterization of any such peptides. The scope of the investigation was narrowed by consideration of the possibility that tyrosine might be largely localized in the end chains and might play an important role in the end-to-end interaction. This possibility arose from the fact that even the most highly purified collagens still contain a small but definite amount of tyrosine (49), which, moreover, appears to be located in some relatively accessible but critical region of the macromolecule, since purification treatments which remove it also result in loss of the capacity to yield ordered fibrous structures of the native type. The probability that tyrosine might play an important role in the end-to-end interaction was also strongly suggested by the work of Bensusan (50), who showed that iodination markedly accelerates the thermal gelation of neutral salt solutions of collagen. Tyrosine is the only amino acid in TC capable of being iodinated, with the exception of histidine, which reacts only very slowly.

A further suggestive piece of evidence was the isolation by Grassmann and coworkers (10) of the tyrosine-containing S_f peptide from enzymatic digests of collagen. It seems very probable that the S_f peptide may, indeed, represent the terminal portion of one of the end chains.

For these reasons the main effort was directed toward determining whether tyrosine-containing peptides are liberated by the action of proteases on the TC macromolecule. Trypsin-treated TC solutions were iodinated with radioactive I^{131}, and the resulting solution was fractionated by paper curtain electrophoresis. The distribution of radioactivity obtained in this way in a control run with trypsin alone, a run with native TC solution after trypsin treatment, and a run with trypsin-treated heat-denatured collagen are shown in Fig. 22. The distribution patterns are quite complex, but it is

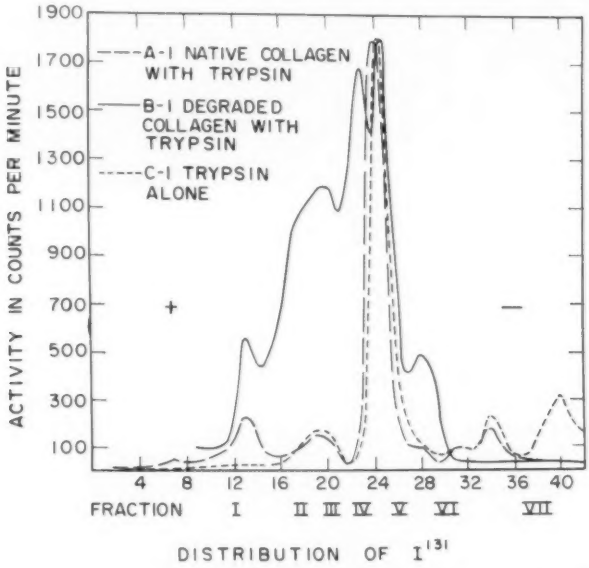

FIGURE 22.—Distribution of I^{131} activity in the effluent from paper curtain electrophoresis of tryptic-treated calfskin collagens. From Hodge, Highberger, Deffner, and Schmitt (46).

clear that trypsin has liberated from both native and denatured TC an acidic peptide fraction (Fraction I) which was not present in the control run with trypsin alone. Control runs with native collagen alone (not shown in the figure) also failed to show any significant activity in the region of Fraction I. The electropherogram for the run with heat-denatured collagen plus

trypsin, after staining, first with ninhydrin (positive reaction indicated by *N*), then with amido-black (positive reaction indicated by *A*), is shown in Fig. 23. It is to be noted that the amount of Fraction I was too small to be

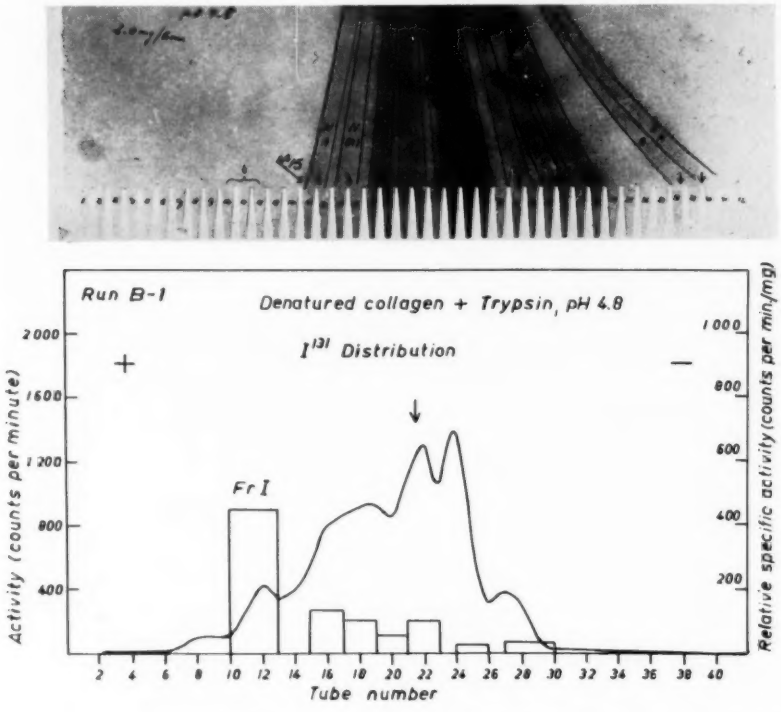

FIGURE 23.—The distribution of I^{131} activity in paper curtain electrophoresis of denatured collagen treated with trypsin (Run B-1 of Fig. 22) together with the relative specific activities of the various fractions indicated in Fig. 22. At top is shown the electropherogram of the same run after staining, first with ninhydrin (positive reaction indicated by N), then with amido-black (A). Note that Fraction I escaped detection by staining with both reagents but has by far the highest specific activity of the various fractions examined. From Hodge, Highberger, Deffner, and Schmitt (46).

detected by either type of staining, but that it was readily detected by its I^{131} activity. The distribution of I^{131} activity in the collecting tubes and the relative specific activities of the various fractions are also indicated. The high relative specific activity found for Fraction I indicated that this peptide must be rich in tyrosine, and this fact was confirmed by two-dimensional paper chromatography of an acid hydrolysate (Fig. 24). As expected from

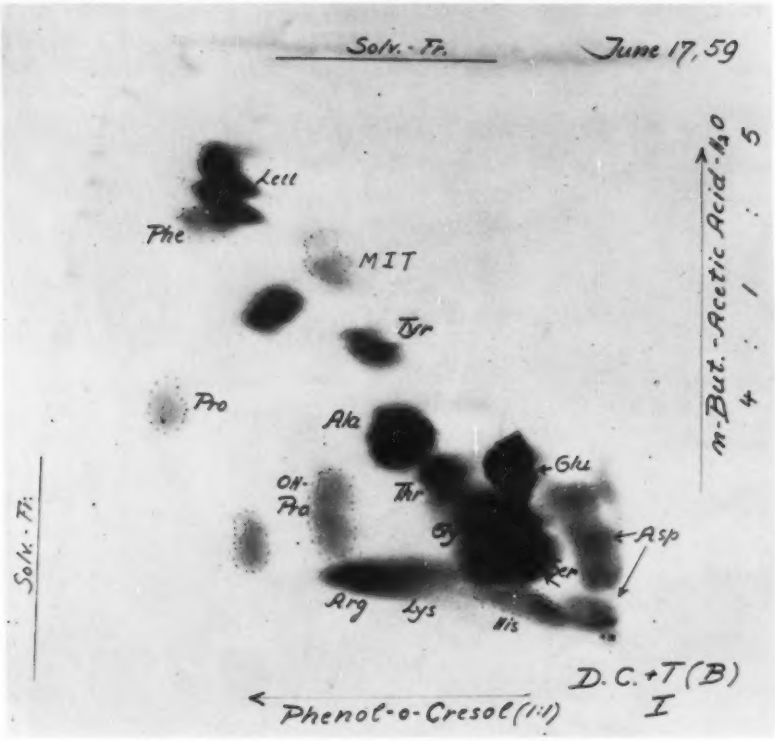

FIGURE 24.—Two-dimensional paper chromotogram of an acid hydrolyzate of Fraction 1 from Run B-1, shown in Figs. 22 and 23. Note the relatively large amounts of tyrosine (Tyr) and mono-iodo-tyrosine (MIT). From Hodge, Highberger, Deffner, and Schmitt (46).

its chromatographic behavior, the fraction is rich in acidic amino acids and relatively poor in basic ones. It also contains some hydroxyproline.

It therefore appears from these results that the action of proteases, such as trypsin and pepsin, on the TC macromolecule, causes the liberation of tyrosine-containing peptides, without affecting the native helical configuration of the macromolecule itself. The results are consistent with the end-chain hypothesis of the mechanism of end-to-end interaction of the TC macromolecule and suggest that the tyrosine residues of collagen may play an important role in such interactions.

CONCLUDING REMARKS

Seven years ago, at the time of the Golden Jubilee Meeting of our Association, I summarized the existing state of our knowledge of collagen. I believe that anyone who compares that paper (51) with the summary of recent work just given cannot fail to be impressed with the great forward strides made in the intervening years.

Scientific progress usually has an autocatalytic effect leading to still greater acceleration, and we may confidently expect even greater advancement in knowledge in the next decade, since work on collagen is now being actively pursued in many laboratories all over the world. This progress will have an important impact on the leather industry, and it must therefore be the task of all of us to follow the great example of John Arthur Wilson and maintain an awareness of these developments to the maximum degree.

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ALCA NEWS

Proceedings, Reports, Notices, and News

of the

AMERICAN LEATHER CHEMISTS ASSOCIATION

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During the months of September and October of this year the Editor-in-Chief will be away from his office. The Associate Editor, Dr. Thomas C. Thorstensen, will assume the duties of the Editor-in-Chief during that period. All manuscripts and correspondence pertaining to manuscripts should be addressed to Dr. Thorstensen at P. O. Box 267, Lowell, Mass.

JALCA GETS AROUND—Officials of the Leather and Footwear Center at Gurjranwala, Pakistan, are shown at the presentation of a bound set of *JALCA* (1927 through 1950) provided through the offices of Dr. Albert E. Chouinard, professor at Lowell Technological Institute, Lowell, Mass.; Kenneth E. Bell, chairman of the LTI Research Foundation's executive committee; and the American Leather Chemists Association.

The background of the cover is reproduced from a U.S.D.A. photograph of pigskin leather by M. C. Audsley.

MINUTES OF THE JOINT MEETING OF COUNCIL AND THE CONVENTION COMMITTEE

June 8, 1961
Shoreham Hotel
Washington, D. C.

The meeting was called to order at 1:30 P.M. with President Henrich presiding. The Council met with the Convention Committee, and the following were present: Messrs. Maeser, Meo, Miller, Stubbings, Tetreault, Turley, Windus, and O'Flaherty and Mrs. Henrich.

The minutes of the March 16, 1961, Council meeting were approved as published.

The meeting was then turned over to Mr. Meo, Chairman of the Convention Committee. Mr. Meo reported plans at length and in detail. The following actions were approved by Council:

It was agreed to publish a pocket-size program 5″ x 7″ in black-and-white, English only, with blank pages for notes. The regular program in good style with abstracts in the three languages will also be published. This program will have a page listing and expressing appreciation to the various firms and individuals who so generously contributed toward defraying the expenses of the meeting.

Council will hold a brief meeting on Sunday night after the Presidential Reception and another meeting on Tuesday at 4:30 P.M.

The registration fee is $20 for members and women, and $35 for nonmembers. It was agreed that tickets for attending only one technical session be provided and be sold for $10 per session. This would apply to students also.

Council approved the printing of 200 extra copies of the August issue of the *Journal*. These would be distributed to foreign members who are not mutual members and also nonmembers who may be interested.

Tickets in strips, with a separate coupon for each event, are to be provided to each registrant.

A list of the foreign registrants to date was read.

The badge was approved as submitted by the Secretary.

The Awards Committee nominations were approved. Dr. Turley is to present the nominees, and President Henrich will make the awards at the banquet.

The meeting then was turned back to President Henrich.

The matter of publishing ALCA-ASTM Methods as "Tentative" was approved.

The charge of 75¢ per copy for Supplements Seven and Eight was approved.

It was agreed that the subscription rate of the *Journal* would remain the same in 1962.

Council approved the President's committee to select a new editor for the *Journal*—Messrs. H. Y. Miller, W. T. Roddy, and I. C. Somerville (chairman). This committee is to report their recommendation for a new editor to succeed Dr. Windus whose three-year term expires March 1, 1962.

The committee on the 1962 John Arthur Wilson Memorial Lecture was advised by the President that the lecturer for 1962 will be announced at the meeting in August.

Mr. F. Klimpl is to be the Convention Chairman for the 1962 meeting.

The following delegates from the ALCA to the International Union of Leather Chemists Societies were approved by Council: President Henrich, President-Elect Stubbings, Secretary O'Flaherty, Messrs. Lollar, H. Y. Miller, Meo, Turley, and Maeser.

Dr. Stubbings nominated Dr. Braunschweig as Chairman of the Tannery Effluents Committee. Council approved.

Dr. Stubbings requested suggestions for someone to assume the chairmanship of the Vegetable Tanning Committee be sent to him.

There being no new business, the meeting adjourned by motion duly passed at 4:30 P.M.

FRED O'FLAHERTY
Secretary

EMPLOYMENT NOTICE

TANNING CHEMIST WANTED—To work on technical and product development program and evaluation of development products. Experience in syntan and resin tannages. B. S. in Tanning Chemistry required. Send résumé in complete confidence (please include salary requirements) to: Professional Relations, Nopco Chemical Company, 60 Park Place, Newark, New Jersey.

DIRECTORY CHANGES

NEW MEMBERS

Antonio G. Ferri, 10 Avenida, 9-37, Zona 1, Guatemala, C.A. Facultad Medicina Veterinaria y Zootecnia, Guatemala, C.A.

Paul D. Finnegan, 131 Butman Road, Lowell, Massachusetts. A. C. Lawrence Leather Company.

Joseph Kochanski, 4211 Sheffield Avenue, Philadelphia 31, Pennsylvania. Thomas B. Harvey Leather Company, Leopard & Wildey Streets, Philadelphia 23, Pennsylvania.

Joseph V. Lukasik, c/o John T. Riddell, Inc., 1259 North Wood Street, Chicago 22, Illinois.

John A. Pierce, University of Arkansas Medical Center, Department of Medicine, 4301 West Markham Street, Little Rock, Arkansas.

Carlos A. Rivera, 11 Avenue "A" 14-52, Zona 2, Guatemala City, C.A. Medicine Veterinary School, University of San Carlos.

Walter H. Sauer, Hartland Tanning Company, Inc., Hartland, Maine.

Adrian J. Stewart, Probst & Cia. Ltda., Apartado Aereo 919, Medellin, Colombia, S.A.

CHANGES OF ADDRESS

Elwin D. Carswell, Rt. 4, Jackson Highway, Milan, Tennessee.

Robert L. Cunningham, 7 Ocean Avenue, Marblehead, Massachusetts.

George Kardos, 421 Lemoyne, Beloeil Station, P.Q., Canada.

E. John Koppany, Compania Industrial de Cuero S.A., Casilla de Correo No. 8, Moron, F.C.N.D.F.S., Argentina.

G. J. Martin, 76 Pomeroy Road, Madison, New Jersey.

ABSTRACTS

The Possibility of Improving the Tensile Properties of Vegetable-tanned Leather by Various Types of Pretannage. E. Heidemann. *Das Leder*, **11**, 294–98 (1960).—The effect of different pretannages and of temperature and concentration of retanning liquors on tensile strength was studied. Pretanning was with Tanigan extra CU, Chromitan (1% Cr_2O_3), Zevalon, Tanigan extra CM, Drasil V, formaldehyde, and a control (no pretannage). Retannage was in 5°Be and 15°Be wattle liquors, both cool (17°–22°) and warm (35°–37°C.). Time of retanning, which was stopped 1–3 days after complete penetration, varied from 5 to 28 days. Retanning was done in tin vessels coated inside with polyethylene by heating the vessel to 200°C., adding polyethylene powder, and rotating. In the 5° liquors there was no significant difference, at the 95% point, between cool and warm retanning for any pretannage, but in 15° liquors the first three pretannages listed above, all of which contain chromium, gave leather that was significantly weaker, at the 99% point, if retanned warm than if retanned in cool liquors. Leathers retanned in cool 15° liquors were stronger than those retanned in cool 5° liquors, however the difference was significant only for leathers pretanned with Zevalon and Tanigan extra CM. When retanned in warm 15° liquors, leathers pretanned in Tanigan extra CU and chrome were significantly weaker, and that pretanned with formaldehyde was significantly stronger, than comparable specimens retanned in warm 5° liquors. The strongest leather was

that pretanned with Tanigan extra CU and retanned in either warm or cool 5°, or in cool 15°, liquors. Thickness changes might explain some of the differences in strength. The 15° liquors caused dehydration and decreased thickness of some leathers and therefore higher calculated tensile strengths, but the reverse was true for other leathers, so it was not clear whether or not strength was influenced by concentration of the vegetable tan liquor. The lower strength of leather pretanned with chrome-containing agents then retanned in warm 15° liquors was caused by displacement by vegetable tannin of sulfuric acid from the chrome complex and damage to the leather fibers by this acid at the higher temperature. I.D.C.

Construction of a New Tannery in Bosany. L. Buriánek and J. Spanko. *Kožařství*, **10**, 143–45 (1960).—This tannery, which processes 4000 tons of salted pigskins annually (60% grain upper, 20% lining, 20% bag leather), consists of two single-story buildings, each 40 x 20 m., for beamhouse and Cr tanning and an adjacent 4-story building (35,500 cu. m.) for finishing, laboratory, and remote control rooms. Separate piping is provided for water at 20°, 40°, and 70°C., and separate drainage for sanitary sewage, industrial wastes, and rain. The beamhouse and tannery have acid-proof tile floors. Concrete lime vats are used. Machinery is operated by remote control using compressed air from a central control room. L.M.

Project for a Vertical Beamhouse in a Tannery. V. Oplustil. *Kožařství*, **10**, 148–50 (1960).—This structure, for 800 calf or 1500 goat per day, measures 19 x 13 m. Skin and chemical storage is on the fourth floor, lime paddles on the third, unhairing, fleshing, and scudding machines on the second, and Cr tannage on the first. A saving of 22% floor space compared to single-story construction is claimed. L.M.

Fifteen Years of Czechoslovak Tanning Industry. M. Tomisek. *Kožařství*, **10**, 161–65 (1960).—A report on new developments in construction of tanneries and in technology. L.M.

Cementing of Soles by Vukoplast DR on PVC Uppers of Shoes. V. Pancoska and B. Suster. *Kožařství*, **10**, 87–89 (1960).—Rubber or leather soles are cemented to polyvinyl chloride (PVC) uppers by means of Vukoplast DR, a two-component butadiene-acrylonitrile cement. Initial joint strength is 3 kg. per 2.5 sq. cm., which does not change up to 70°C. Ten parts of the cement are mixed with 1 part stiffener (composition not given), and both surfaces must be coated within 30 min. after mixing. Joining is done after drying for 20 to 35 min., at a pressure of 4 kg. per sq. cm. Irradiation of one of the surfaces by dark infrared for 50 to 100 sec. activates coatings that are 5 to 8 hr. old. L.M.

Between the Firsts of the World. Anon. *Kožařství*, **10**, 97–101 (1960).—Progress of leather and allied industries in Czechoslovakia between 1945 and 1960 is described. In 1960, 80 million pairs of shoes were made, and 28 million exported. All the leather was made in Czechoslovakia. Rolling of sole leather on an automatic calender has been introduced. L.M.

Application of Cements on Leather, Textiles, and Rubber. M. Zeman. *Kožařství*, **10**, 121–23 (1960).—Many types of shoe cement are objectionable hygienically. In the "acetone solvent" (a mixture of acetone, methyl acetate, and methanol) more than 1% of aldehyde is objectionable. Solvent naphtha should not contain more than 6% benzone and 12% total aromatics. L.M.

Leather Analysis in Relation to Czechoslovak Standards. L. Minarik and D. Kokes. *Kožařství*, **10**, 44–46, 68–71 (1960).—Samples are conditioned at 65°C. Resistance to bursting, stitch tear, tongue tear, and bolt tear is discussed. In determining water absorption the Kubelka apparatus is used; 18° ± 2°C. must be maintained. The static water permeability test has been found unsuitable; a new apparatus for simultaneous determination of dynamic permeability and water absorption is being developed. Water vapor permeability should be 1500 mg. per sq. dm. per day to permit transport of sweat through shoes. Because of increased use of resin finishes the averages for glazed side upper and glazed kid have dropped from 454 mg. to 143 mg., and from 544 mg. to 261 mg., respectively, from 1956 to 1958. The light stability test is too slow. The acetic acid test for complete tanning, useful for straight vegetable leather, is not applicable to Cr-vegetable leather; a transparent center layer in the cut, without swelling, does not indicate insufficient tanning. Hydrothermal stability is measured by decrease in bursting strength after exposure to 100% relative humidity for 4 hr. at 50°C. for vegetable leather or at 60°C. for Cr leather. Fat is determined by extraction with $CHCl_3$ or petroleum ether; ashing is done at 600°C.; H_2O-soluble matter is extracted at 45°C. The pH value of the H_2O extract is determined in a quartz apparatus. Determination of leather substance in Cr-vegetable leather depends on the evaluation of the Cr tanning compound. L.M.

Damage to Skins by Bacteria in Soaking. A. Orlita. *Kožařství*, **10**, 42–43 (1960).—Dry-salted goatskins, soaked in 800% water at 28°C. to intensify bacterial damage, had a putrid odor in 2 days, and perforation occurred in 3–4 days. Organisms chiefly responsible were *B. subtilis*, *mesenthericus*, and *anthracoides*. Concentrations (in %) of disinfectants needed to prevent perforation for 5 days (goatskin) or 7 days (salted steerhide) were: *p*-nitrophenol, 0.15; tetramethyl thiuram disulfide, 0.25; *p*-Cl-*m*-cresol, 0.08; *p*-Cl-*o*-cresol, 0.05; Na penta-Cl-phenolate, 0.03–0.05; Na_2SiF_6, 0.10; penta-Cl-phenol, 0.05; 5 antibiotics, 0.001–0.015. Penta-Cl-phenol is considered best of the chemical disinfectants; use of 0.20% of a 10% solution is recommended. *p*-nitrophenol and tetramethyl thiuram disulfide are more active against molds than bacteria. The antibiotics are much more active, but they are expensive. Tetracyclin and oxytetracyclin are more active than chloramfenicol and streptomycin. In practice, a 1:1 combination of tetracyclin or oxytetracyclin with either chloramfenicol or streptomycin, along with Na penta-Cl-phenolate, probably is best. L.M.

Radioisotopes in the Tannery. A. Blažej. *Kožařství*, **10**, 5–10 (1960).—Use of radioisotopes in tannery research and technology is discussed. Fibrogenesis of collagen *in vivo* has been studied by feeding labelled glycine to rabbits and determining it in procollagen and collagen. The functions of trace elements have been followed. Radioisotopes showed that fluorosis of cattle

was caused by a large nearby Al plant. Radiochromatography can be used for determining amino acids in collagen hydrolyzates. Halogen radioisotopes can be substituted for H in heterocyclic amino acids, facilitating determination of collagen from proline and hydroxyproline. The influence of radioisotopes on the band structure of collagen protofibrils changes the reactivity of collagen, which might have great technological importance. X-ray irradiation lowers the degree of crystallinity of wet collagen by 70–100% but has no effect on dry collagen. Progress of tanning can be followed by histoautoradiographic methods. Hides have been preserved successfully with ^{137}Cs. The mechanism of unhairing and action of clothes moth enzyme on keratin can be studied using ^{35}S and ^{45}Ca. Biosynthesis of tannins and mechanism of polycondensations of syntans can be studied with ^{14}C. Ionizing radiations can be used for effecting large-scale condensations. Tannage by syntans has been followed by means of radioisotopes of S, and Cr tannage by ^{51}Cr. Radioisotopes of N are suitable for studying dyeing. Radioisotopes can be used to vulcanize plastics used in finishes. Static electricity is easily overcome by such isotopes.

L.M.

Sole Leather Production in the USSR. M. Spicka. *Kožařství* **10,** 113–16 (1960).—The standard method of Cr-vegetable tannage is described. Extensive full-scale comparisons have demonstrated the superiority of this combination tannage to straight vegetable tannage. The best procedure is to follow the Cr pretannage with vegetable tannage in a drum in 3 stages. Salted hides are washed briefly in a drum, soaked 1 to 2 days, and limed in 3 or 4 pits with 600% liquor, a minimum of 10 g. CaO per l., and a maximum of 0.8 g. Na_2S per l. The mechanically prepared pelts are washed 45 min. in running water, delimed thoroughly with 2% $(NH_4)_2SO_4$ in 150% water for 6 hr., washed in a drum with lattice door for 45 min., and pickled 8 to 10 hr. with 1% H_2SO_4 in 100% water containing 60–70 g. NaCl per l. Cr pretannage is done with 40% basic glucose-reduced liquor, equal to 0.4–0.6% Cr_2O_3 for heavy, rigid leather, or up to 1.2% for flexible types, added to the pickle liquor. After 14 hr., 0.2% Na_2CO_3 is added, and drumming is continued 2 hr. The chromed hides are horsed 24–48 hr.; some types are shaved. Vegetable tanning is done in 3 liquors: (1) 160% of liquor from (2) containing 6% tannin, pH 4.9, 30°C., 24 hr.; (2) spent liquor is sewered and liquor from (3) containing 13% tannin is pumped onto the hides; (3) after 48 hr. the spent liquor is pumped to (1) and replaced by 180% of fresh liquor, 18% tannin, pH 3.8, 43°C. for 48 hr. Tannin given equals 20–30% on pelt weight for rigid leather, and 26–28% for flexible. The blend contains 85% vegetable tannin, predominantly oak with some willow and spruce bark extracts and 15% syntans for rigid leather, and 70% vegetable tannin, mostly willow, with 30% syntan for flexible leather. Tanned leather is rinsed, horsed, washed, pressed, and loaded with 1.0–1.5% Epsom salt and 2% glucose in a heated drum at 35°–40°C. for 35–40 min. Shoulders and bellies for inner soles are often treated with 2–4% potash alum for 20–30 min. before loading, to enhance resistance to sweat. The leather is stuffed at 50°–60°C. with a mixture of animal and vegetable oils for 30–40 min., piled 24 hr., set out, hung for 2 hr. at 40° ± 2°C. and 45 ± 2% relative humidity in an air current having a velocity of 1.5 ± 0.5 m. per sec., struck out again, and hung for 90 min. more under the same conditions. The leather is oiled off and dried for 24–48 hr. (10 hr. for thin leathers) at 50° ± 2°C. and

40 ± 2% relative humidity in air at the above velocity. Bends are calendered twice after damping to 18% water content. A semiautomatic finishing line, turning out 1700 tons per year of sole leather, is described. Soviet sole leather has good quality but an objectionable dirty green color caused by Syntan AN (sulfonated anthracene) made in Fe apparatus. The quality of shoulders and bellies is not up to that of the bends. The composition of the tanning blend should be changed to employ more wattle and quebracho extracts.

L.M.

World Development of Sole Leather Technology. A. Leska. *Kožařství*, **10,** 145–47 (1960).—The highest permissible temperature for vegetable tannage is 40°C. A pretannage is necessary for the rapid tanning of sole leather. Cr pretanning is best, but pretannages with Al, syntans, polymetaphosphates, and HCHO are also possible. Cr pretannage, employing 0.5–0.7% Cr_2O_3, results in a 10% increase in abrasion resistance. Cr retannage is done in 60% pickle liquor using 42% basic Cr liquor for 7 hr. followed by 0.1% Na_2CO_3 for 1 hr. Tannage is done in 12 pits. The tannin concentration can be raised from 30 g. to 154 g. per l. within 20 days. A blend of 50% vegetable tannin and 50% syntan gives good quality leather in 50 days. Generally 30% tannin on the pelt weight is not enough. Temperature must not exceed 30°C. Pretannage with a 1:6 mixture of HCHO and glyoxal at pH 9.5 and retannage with hardwood lignin extract also gives a good leather. Bated skin is brought to pH 9.5 in the paddle with $NaHCO_3$ and Na_2CO_3, tanned in a running drum with the aldehydes for 5 hr., let stand overnight, and brought to pH 3.8 with H_2SO_4. Retannage is done in 3 pits with sodium lignosulfonate, 7°Bé and 50°C. in the first, 9°Bé and 50°C. in the second, and the same liquor cooled to room temperature in the third. The resulting leather is very flexible and has a degree of tannage of 48 to 64. The process takes 7 to 8 days. Pretannage with a 5% solution of dialdehyde starch (Beebe *et al.*, *JALCA*, **54,** 678 [1959]) at pH 8.0 is described. Retannage in vegetable liquors at pH 4 for 3 to 5 days generally is sufficient. Zr pretannage gives a leather that is very resistant to abrasion but with high water absorption. The pelt is pickled to pH 1.0–1.8, pretanned 48 hr. with Zr tanning compound, neutralized with Na formate to pH 3.0, and with Na_2CO_3 to pH 4.2–4.5. The leather is piled 24 hr. and then vegetable-retanned. The high water absorbency of this and other combination-tanned sole leathers can be overcome by impregnation, e.g., with complex salts of aliphatic amines and phenol or cresol in organic solvents. The air permeability of leathers thus treated is normal, and water absorption is within permissible limits, 3–7%, 10–12%, and 22–28% after 1, 3, and 24 hr., respectively. Solvent tannage has passed the pilot-plant stage. It is being used on a large scale for upper leathers and is being introduced into sole leather tannage. L.M.

Polarographic Determination of Sulfur Compounds in the System: Sulfide-Cysteine-Cystine. A. Blažej, J. Ceřnak, J. Stefanec, and B. Síles. *Kožařství*, **10,** 139–42 (1960).—Methods are described for polarographic determination of sulfide, cysteine, and cystine in used lime liquors. Five sole leather lime liquors aged 10, 17, 18, 20, and 22 days contained 4.7, 7.1, 5.6, 3.3, and 4.4 g. total sulfide sulfur per l. by iodometric titration, and 4.8, 7.0, 5.5, 3.2, and 4.45 g. per l. by polarography. The cysteine contents were: trace, trace, 0.07, 0.09, and 0.12 g. per l. Cystine was absent. L.M.

Solvent Tannage. H. Weber, M. Tomisek, and R. Exner. *Kožařství*, **10,** 166–68 (1960).—Pilot-plant experiments are reported. Two drums, each 2 x 1.8 m., 8 rpm, with reflux condenser are used. The solvent, ethanol, is recovered by distillation in a column with capacity 1000–1200 l. per hr. Delimed, bated or pretanned, well sammied pelts are flooded with ethanol in the drum, and after 20 min. an ethanol solution of an unsulfonated resin (syntan), a pyrocatechol novolak, is added in 3 parts at 1-hr. intervals. The stock is drummed continuously for 10 hr., and then 10 min per hr. for another 10 hr. The spent liquor is pumped to a tank. Water is added to the drum at 20°–30°C., and the stock is drummed at least 30 min. The diluted liquor is pumped to the tank. More water is added to the drum and removed after 30 min. The mixed spent liquor and washings should not contain over 10% ethanol, which is recovered by distillation. Excess resin in the spent liquor is precipitated by dilution, and recovered. The tanned leather is finished normally. Resin equal to 25% pure tannin on the pelt weight is required. For improved appearance and firmness, the leather is retanned with aqueous vegetable tan liquors, 63° Barko., for 2–3 days. Sole leather thus produced had apparent density 1.0; water absorption after 2 and 24 hr., 34% and 41%, respectively; hydrothermal stability, 92%; ash, 0.8%; fat, 1.2%; water-soluble matter, 8.3%; leather substance, 76%; pH of water extract, 4.2. Some 7000 kg. of experimental leather has been produced. Tanning time is 3 to 4 days, and floor space required is 25% of normal L.M.

Leather Impregnation. A. Leska. *Kožařství*, **10,** 169–71 (1960).—A critical review with 19 references. L.M.

Investigations on Pelt Swelling. II. I. Kerese. *Bőr- és Cipőtechnika*, **10,** 67–70 (1960).; *Hung. Tech. Abstr.*, **13,** 20 (1961).—The effect of various electrolytes added to the lime liquor on the stiffness of the pelts has been investigated by the author's recently developed method (abstr. *JALCA*, **55,** 361 [1960]). The experiments demonstrated the specific influence of the ions and the role played by concentration. Lots were investigated in factory production, and a relationship between the stiffness of the pelt and the quality of leather was found. H.B.M.

Treatments for the Prevention of Iron Rot in Leather. I. B. C. Paul. *J. Indian Leather Technologists' Assoc.*, **9,** 7–9 (1961).—Pieces of leather, variously treated, were tacked together and exposed to various conditions (room atmosphere, tropical chamber, repeated wetting and drying, etc.) for 12 to 18 months, after which the leather was examined for iron contamination, and the tacks for rusting. Treatments with stearin, paraffin, Al stearate, Cr oleate, Cr retannage, and Calgon treatment conferred varying degrees of resistance to Fe contamination and rusting. H.B.M.

A Rapid Vegetable Tannage for Hides and Skins. K. V. Vaidyalingham. *J. Indian Leather Technologists' Assoc.*, **9,** 10–11 (1961).—Delimed pelts are tanned with HCHO, brought to pH 4 with organic acid, drum-tanned with 3% to 5% of a syntan, and then with vegetable tannins for 24 hr. The leather is stuffed and finished for insoles and straps. The yield is about 50% on pelt weight. H.B.M.

Some of the Factors Affecting the Processing of Chrome-retanned Upper Leather. P. K. Ghosh. *J. Indian Leather Technologists' Assoc.*, **9,** 12–17 (1961).—A general discussion, emphasizing the need for careful neutralization before vegetable retanning. The same end can be attained by treatment with auxiliary syntans and by a preliminary fatliquoring before retanning. H.B.M.

Production of Patent Leathers Finished with Polyurethane Lacquers. W. Speicher. *J. Soc. Leather Trades Chemists,* **45,** 104–23 (1961).—A lecture. S.D.

Investigations on Bating. VII. Some Microscopical Observations. M. Dempsey and G. H. Green. *J. Soc. Leather Trades Chemists,* **45,** 92–103 (1961).—The effects on fiber structure of the following pretanning treatments applied to dry-salted goatskins soaked back in the tannery were investigated: sweating, liming, and bating; enzyme unhairing, liming, and bating; and liming, bating, and reliming. At each stage in the various processes samples were removed from the pieces of skins and examined microscopically. All the skins were then processed to the chrome crust, with examination after pickling, in the blue, after fatliquoring, and after air-drying or acetone dehydration. Photographs show grain and corium sections of the chrome crusts. The observations of examinations at the various process stages are listed and discussed. S.D.

The Effects of Organic Acids on the Fixation of Chromium and Zirconium by Chemically Modified Collagen. R. L. Sykes and D. A. Williams-Wynn. *J. Soc. Leather Trades Chemists,* **45,** 83–92 (1961).—The effects of eight carboxylic acids as masking agents on the fixation of chromium and zirconium salts (sulfates and chlorides) by collagens were studied. The collagen substrate consisted of 2-inch squares of goatskin corium. A portion of this substrate was used without further chemical treatment (control), and other portions were treated to modify the polar side chains by esterification, carboxylation, and acetylation. From the results obtained, the following conclusions were reached: although some aspects of the chemistry of the zirconium and chromium compounds are similar, the mechanism of the two tannages apparently are not the same. Chrome tannage undoubtedly involves the reaction of charged carboxyl groups with the metal to form a coordination complex. The evidence on the mechanism of zirconium tannage is contradictory, and further investigations seem to be required for its elucidation. S.D.

Bilateral Structure of Wool. M. Horio, T. Kondo, K. Sekimoto, and A. Teramoto. *Z. Naturforsch.*, **15b,** 343–45 (1960); abstr. in *J. Soc. Dyers Colourists,* **77,** 134 (1961).—Histochemical determination of the isoelectric points of the two cortex components of wool dyed with acid and basic dyes gave values of 6.75 and 6.40 for the acidophilic part on the inside of the curvatures for Merino and Corriedale wool, respectively. For the basophilic part on the outside of the curvatures the values were 5.90 and 6.15. The acidophilic part absorbed more than the basophilic part at 3130 Å, while the latter absorbed more at 2800 and 2650 Å. The hair root behaved like the basophilic part toward basic dyes; the acidophilic part appeared at one-third of the distance between the root and the skin surface. C.L.D.

Microscopic, Microchemical, and Physical Examination of the External and Internal Structure of Wool. II. Experimental Investigation of the Bilateral Structure and Its Relation to Fiber Variations and Damage. R. Ritter and H. Reumoth. *Z. ges. Textil-Ind.*, **62,** 342–50 (1960); abstr. in *J. Soc. Dyers Colourists*, **77,** 134 (1961).—Diamine Sky Blue FF is especially suitable for differentiating the bilateral structure. Wool slubbing was dyed with 1% of the dye, dried, and treated with 1% Na isopropoxide in isopropanol, the alcohol was evaporated, and the fiber was embedded in oil of bergamot. The ortho-cortex became colorless, while the para-cortex remained blue, after 12–24 hours. When the wool was dyed in a cold bath with Procion Brilliant Red 2BS, and 1% NaOH added, the ortho-cortex was colorless to light yellow and the para-cortex yellow to orange, regardless of chemical or physical damage to the wool. Oxidation by H_2O_2 attacks both ortho- and para-cortex. The bilateral structure of wool is also rendered visible by treatment with a methanolic solution of LiBr, the scale structure being retained. LiBr seems to protect the fiber during aftertreatment with alkali. Apparently, appearance of the bilateral structure indicates that the fiber has previously been damaged. C.L.D.

Localization of Arginase in Rabbit Skin. S. Rothberg and E. J. Van Scott. *Nature*, **189,** 823–33 (1961).—Arginase in rabbit skin is largely localized in the epidermis. C.L.D.

A Fatty Acid–Protein Complex in Human Hair. A. W. Holmes. *Nature*, **189,** 923 (1961).—A protective substance exists in human hair which maintains it intact during papain digestion. This protective substance has been isolated from ethanol extracts of hair by electrophoresis on polyurethane sponge in dilute acetic acid at pH 2.5. It consists of 20–30% fatty acid and 60–70% protein. The latter yields substantial amounts of lysine but very little cystine. Treatment of alcohol-extracted hair with an alcoholic solution of the complex reduces the rate of breakdown of hair by papain. This is not due to enzyme inactivation, since the degradation of casein by papain is not affected by the presence of the complex. C.L.D.

Thermo-reversible Denaturation of Eucollagen in Solution. N. T. Crosby and G. Stainsby. *Nature*, **190,** 80–81 (1961).—Solutions of eucollagen, formed by solution of mature collagenous tissue in weakly acidic media after a cold pretreatment in alkali, possess a high specific viscosity over the temperature range 5°–25°C. and a very much lower value at 35°C. and higher temperatures. The high viscosity at low temperatures suggests that eucollagen has a rigid, rod-like form in solution, while the relatively low viscosity at 35°C. and higher temperatures reflects the flexible nature of the gelatin molecules which are formed rapidly and irreversibly under such conditions. At intermediate temperatures (for example, 30°C.) the initially high viscosity falls with time, and on recooling to 20°C., the solution shows a marked and rapid rise in viscosity. The maximum possible contribution to the viscosity from aggregation of derived gelatin is far smaller than the observed changes in the viscosity of soluble eucollagen at 20°C. after a period at 30°C. It is presumed that the structural disorganization on heating eucollagen in solution at 30°C. proceeds in two steps, the first of which is partially reversible by cooling, while the second gives rise irreversibly to gelatin. C.L.D.

Mechanism of Collagen Synthesis. G. B. Gerber and K. I. Altman. *Nature*, **189,** 813–14 (1961).—A mechanism is proposed for the biosynthesis of collagen which could account for the experimental data available at present. This mechanism is based on the premise that collagen is synthesized by an enlargement of the pre-existing collagen fiber by means of the addition of amino acids or peptide residues, analogous to the mechanism proposed for biosynthesis of hepatic glycogen. The proposed process is unlike that visualized for globular proteins, which are thought to be synthesized by one continuous process. C.L.D.

Collagen. Jerome Gross. *Scientific American*, **204,** No. 5, 121–30 (1961). —A lucid, superbly illustrated account of the structure and mode of formation of collagen fibrils. H.B.M.

Biological Characteristics of Indian Hides and Skins. I. Uttar Pradesh. S. K. Sarkar, D. K. Das, S. K. Mitra, Y. Navudamma, and B. Bhaskaran. *Bull. Central Leather Research Inst., Madras*, **7,** 249–75 (1961).—Skins of different breeds, sex, age, and state of health, from various regions of this province, were examined histologically for hair density, depth and inclination of follicles, percentage of coarse hairs, thickness of epidermis, grain layer and corium, tightness of grain, characteristics of fiber structure, gland tissue, and distribution of body fat. An assessment of the leathermaking properties of the several types is made. H.B.M.

Use of Margosa Bark for E. I. Tanning. K. R. V. Thampuran and E. C. Mathew. *Bull. Central Leather Research Inst., Madras*, **7,** 276–77 (1961).—The bark of this abundant, rapid-growing tree (*Melia azadirachta*) contains about 15% tannin (dry basis), tannin/soluble matter 0.59, pH of analytical solution 4.8. The tannin is of the condensed type. Goatskins tanned in the laboratory with margosa bark compared favorably with those tanned with avaram. H.B.M.

The Manufacture of Picking Bands. A. K. Mukherjee. *J. Indian Leather Technologists Assoc.*, **9,** 56–58 (1961).—A process is described for successive tannages with sulfur (pickle followed by $Na_2S_2O_3$), oil, and quebracho. H.B.M.

Application of Sugar Cane Wax in Shoe Polish. B. C. Paul. *J. Indian Leather Technologists' Assoc.*, **9,** 59 (1961).—Refined cane wax (sp. gr. 0.986, m.p. 73.5°C.) was used to replace carnauba wax in a polish containing 10 g. paraffin, 1 g. bee wax, 7 g. cane wax, 45–50 ml. turpentine oil, and 0.5 g. dye. H.B.M.

The Technique of Suede Leather Manufacture. E. Luescher, *Australian Leather Trades Rev.*, Oct. (1960); *Tanner* (India), **15,** 281–84, 321–23 (1961).—To ensure open fiber structure, splits for suede should be taken off before tanning, and relimed. Cationic Cr tannage is preferable for good dyeing properties. A tanning process is described in which unpickled stock is tanned

first with 8% basic Cr alum (2% Cr_2O_3) and 0.5% of a cationic fatliquor in 60% float for 1 hr. at pH 3.4; then 100% H_2O is added, and tanning is continued 2 hr. After shaving, the stock is retanned with 50% basic Cr sulfate (2% Cr_2O_3) and 0.3–0.5% cationic fatliquor and fatliquored in the exhausted Cr tanning bath with a proprietary fatliquor. The cationic fatliquor is said to have a dispersing action on Cr salts, resulting in an even uptake of Cr and consequent level dyeing. Fatliquoring should produce a leather that is easily wet back. Neutralizing agents that form complexes with Cr, and anionic wetting agents and fatliquors tend to reduce the affinity of the leather for anionic dyes. Use of various proprietary materials as dyeing assists is described. Procedures for making garment suede water-repellent by use of Cr stearato chloride or silicones are given. H.B.M.

Different Permeability of Cuticular Sheath in Normal and Guard Keratin Fibers. R. de la Burde. *Nature*, **190,** 420–22 (1961).—The differences in coalescence of cuticular membrane between fibers of normal and guard hairs of rabbit skins were characterized on the basis of their resistance to the penetration of aniline black and acridine orange. The guard hair is considerably more resistant to the penetration of acridine orange and aniline black than the normal hair. The impermeable membrane in guard hair is the cuticular sheath; wherever the cuticle was penetrated by the compound, the staining or fluorescence was equally distributed throughout the cortex and medulla. The rate of changes in the permeability of cuticular sheaths in normal and guard hair exposed to the aniline dye in successive treatments suggests that the treatment modified progressively the protein structure. The differences in the properties of cuticular sheaths of normal and guard hairs can be explained by the varying extent of keratinization, the principal factor being the degree of disulfide cross-linkage in the cuticle of both fibers. C.L.D.

Studies on Cystine in Wool. VI. Relationship Between Thiol Groups and Supercontraction. Y. Nakamura, Y. Nemoto, and M. Oku. *J. Soc. Textile Cellulose Ind. Japan*, **16,** 852–58 (1960); abstr. in *J. Soc. Dyers Colourists*, **77,** 181 (1961).—Studies on the relationship between the thiol group and supercontraction of wool in phenol solution indicated that supercontraction depends more on the total thiol group content than on cross-linkages between keratin molecules, and increase of supercontraction found in alkaline phenol solution could be caused by increase in thiol groups formed by hydrolysis of disulfide bonds. C.L.D.

Effect of Preparation and Type of Dye on Leather Dyeing. V. Pektor and J. Ondrácek. *Veda a Vyzcum v Prumyslu Kozedelnem*, **5,** 73–100 (1958); abstr. in *J. Soc. Dyers Colourists*, **77,** 188–89 (1961).—Leathers of a wide variety of tannages and retannages were dyed at pH 3.0, 4.5, and 6.0 with each of the dyes Chrome Leather Brown 3GN, Alizarine Chrome Red G for Leather, Koregal Blue GG, and Koranil Brown ER. Information is given on levelness, intensity, exhaustion, effect of electrolytes, and fastness to water, fatliquor, and light. C.L.D.

PATENTS

Waterproofing Leather Brit. Pat. 847,832. Wauqiez S. A., H. Filed Feb. 26, 1957.—Tanned leather is made water-repellent while remaining air-permeable by treatment with one or more amines of the general formula $R.NH_2$, where R is an aliphatic radicle containing 8–22 carbon atoms, or one or more diamines. The amines may be wholly or partly neutralized by acid residues in the leather resulting from tanning, or the amines may be neutralized with acid before or after incorporation in the leather to ensure that the *p*H value of the treated leather will be 3.5–5.0. Specified acids are acetic, formic, lactic, hydrochloric, sulphuric, sulphurous, phosphoric, oleic, stearic, abietic, resinic, and naphthenic acids. The amines, which may be used in the form of their salts with acids, may be applied as solutions in organic solvents, or as emulsions. There may be added one or more water-repellent substances soluble in the same solvent as the amine or amine salt, e.g. mineral, vegetable, or animal oils, wax, paraffins, oleates, stearates, naphthenates, or resinates. In examples: (1) zirconium-tanned leather is soaked in a solution prepared by adding to a heated ethyl alcohol-trichlorethylene solution of amines having aliphatic carbon chains of 16–18 carbon atoms, about half being saturated and the remainder unsaturated, first sulphuric acid, and, after the exothermic reaction is completed, acetic acid, colophony, petroleum jelly, and white spirit. The leather after draining and wiping to remove excess, is hung for 2 days in a damp atmosphere and then wiping to remove excess, is hung for 2 days in a damp atmosphere and then dried to a moisture content of 15–18%; (2) zirconium tanned heavy leather is soaked in a solution prepared by adding, first sulphuric acid, then colophony to an ethyl alcohol-trichlorethylene solution of higher aliphatic amines mainly composed of C_{18} chains of which two thirds are unsaturated. The treated leather is completely dried, soaked in cold water, and re-dried to a moisture content of 15–18%; (3) as in (2) but sulphuric acid may be replaced wholly or in part by phosphoric acid, and part of the colophony by oleic, stearic, or naphthenic acid; (4) vegetable tanned leather is treated as in Example (2); (5) powdered tartaric acid, phenol, and powdered colophony are added to a solution of trichlorethylene of higher aliphatic amines prepared from a mixture of tallow and oleine, and zirconium-tanned cow leather is soaked in the resulting solution, dried, immersed in water, and again dried to a moisture content of 15–18%.

Waterproofing Leather Brit. Pat. 848,838. British Leather Manufacturers' Research Association. Filed May 6, 1958.—Leather is waterproofed by applying thereto an organic solvent solution of up to 15% of the total weight of the solution of one or more siloxane resins and a mutually compatible natural or synthetic high molecular-weight organic elastomer, the elastomer being present in amount such that the viscosity of the solution is at least 0.2 poise at room temperature. Elastomers specified are natural rubber, butyl rubber, polyisobutylene and a styrene-butadiene copolymer, preferably having molecular weights of at least 5000, and desirably in excess of 20,000. In

series of tests, strips of chrome-tanned leather were dipped in white spirit solutions containing varying amounts of siloxane and natural rubber or polyisobutylene for periods ranging from 4 to 256 minutes: the solvent was allowed to evaporate and the treated strips were then conditioned in a room at 21°C. and 70% relative humidity and tested for waterproofness.

Tanning Leather. Brit. Pat. 845,644. Farbenfabriken Bayer A. G. Filed Jan. 29, 1958.—Leather is prepared by tanning pelts and hides, e.g. sheep, goat or calf pelts and cow-hide, with a synthetic tanning-agent consisting of a phenol-formaldehyde resin containing sulpho groups prepared by condensing a phenol with formaldehyde in the presence of an alkali metal hydroxide until a polymer containing 2–10 monomeric units is obtained, neutralizing with sulphur dioxide and further condensing at a *p*H of 5–7 until water solubility is attained. As phenols which may be used are mentioned phenol, cresols, dihydroxydiphenyl sulphones, dihydroxy diphenyl dimethyl methane, pyrocatecol, crude cresols and empyrenmatic oil.

Waterproofing. Brit. Pat. 847,414. Monsanto Chemicals Ltd. Filed Jan. 16, 1958.—Materials such as textiles, leather, paper, cardboard, masonry, wood, concrete and metals are rendered water-repellent by treatment with a silicone and a catalyst obtained by reacting an inorganic metal salt, such as the chloride of titanium, zirconium, aluminum, tin, calcium, potassium, sodium or lithium, with an amine such as an ethanolamine or *iso*butylamine and, if desired, with a polyhydric alcohol such as 1:3 butanediol. The silicone may be an aqueous silicone emulsion (*see* Group IV (a)). The silicone and the catalyst may be applied together, or separately in either order. Specifications 723,989, 894,989, 804,990, 812,505 and 823,760 are referred to.

Fabrics Coated with Silicone Rubber Compositions. Brit. Pat. 847,837. Wacker-Chemie G.m.b.H. Filed March 18, 1957.—A leather-like product prepared by applying to a flexible support a room temperature vulcanizing silicone rubbed composition; the coating is given a smooth or embossed surface during or after the application of the coating, and is then vulcanized at room temperature. The composition may be produced as in Specification 841,825, and may contain an organo-hydrogen-polysiloxane as cross-linking agent, a dialkyl tin diester or a dialkylamine as catalyst, and a vinyl polymer, e.g., polyvinyl chloride. A matrix of which the surface is smooth or embossed with a negative relief of the desired embossed effect may be coated with the silicone-rubber composition, the flexible support material applied thereto, and the flexible material carrying the silicone rubber composition stripped from the matrix after vulcanization. Suitable support materials are natural leather, and cotton fabrics. A suitable matrix medium is hard bitumen. Specification 765,774 also is referred to.

Synthetic Tanning Agents. Brit. Pat. 855,571. Farbenfabriken Bayer A. G. Filed April 2, 1958.—Synthetic tanning agents, which blend with other

synthetic or vegetable tanning agents, are obtained by dispersing a condensation product of an aldehyde with a mono- or polyhydric phenol into a mixed condensation product of a polynuclear aromatic sulphonic acid, a halogenated phenol and an aldehyde. In an example, calf skins are drummed in a liquor to which has been added an aqueous solution of a tannin prepared by dispersing an alkali-catalysed empyreumatic oil-formaldehyde condensate into a mixed condensate of naphthalene sulphonic acid, *o*-chlorophenol and formaldehyde. The resulting leather is yellowish, very full and has a good feel. Specifications 965,374, 747,675, 799,224 and 855,572 are referred to.

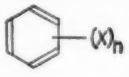
Synthetic Tanning Agents. Brit. Pat. 855,572. Farbenfabriken Bayer A. G. Filed April 3, 1958.—Synthetic tanning agents are obtained by further condensing mixed condensation products of sulphonic acids of polynuclear aromatic hydrocarbons, halogenated phenols and aldehydes with mono- or dihydroxy phenols and aldehydes in an acid medium. In an example, goat skins are drummed in a liquor to which has been added an aqueous syrup of a tannin prepared by further condensing a condensate of naphthalene sulphonic acid, a mixture of *o*- and *p*-chlorophenols and formaldehyde with empyreumatic oil and more formaldehyde. The resulting leather is a yellowish brown, has a soft handle and is very full. Specifications 747,675, 799,224 and 855,571 are referred to.

Waterproofing Leather. Brit. Pat. 858,024. Wacker-Chemie G.m.b.H. Filed Nov. 21, 1957.—Leather is rendered water-repellent by treatment with an organopolysiloxane composition and a water-soluble zirconyl salt. The polysiloxane is of the general formula $R_nSiO_{\frac{4-n}{2}}$, in which R represents a monovalent hydrocarbon radical, e.g. methyl, ethyl, octadecyl, phenyl, anthracyl, tolyl, methylnaphthyl, benzyl, phenylethyl, cyclobutyl, cyclohexyl, vinyl or octadeceynl. and n is from 1.0 to 2.9. The zirconyl salt may be zirconyl chloride, zirconyl acetate, zirconyl nitrate, zirconyl sulphate, zirconyl carbonate, basic zirconyl salts such as $Zr_2O_3Cl_2$, or zirconyl ammonium carbonate. The organopolysiloxane may be applied as a solution in an organic solvent, e.g. benzene, toluene, xylene or perchlorethylene, containing 5 to 15% by weight of polysiloxane, and the zirconyl salt as an aqueous solution containing 0.1 to 5% by weight of zirconium, which may be buffered with an alkali metal acetate. The polysiloxane may also be applied in the form of an aqueous emulsion containing an emulsifying agent. The two materials may be applied simultaneously, by the use of an emulsion of the organopolysiloxane and zirconyl compound, or, if the organopolysiloxane is water-soluble, of an aqueous solution of the two. They may also be applied separately in either order.

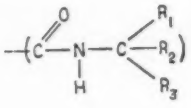
Leather; Fatting Skins. Brit. Pat. 852,986. Ushakoff, A. E. Filed Jan. 13, 1959.—In the manufacture of leather, skins, especially after tanning, are fatted by the application of a fatting agent, or a solution thereof in an organic solvent, to the surface of a skin which has previously been wetted with an inert organic solvent in which the fatting agent is soluble and subsequently drying

the skin, preferably by heating to a temperature above the boiling point of the solvent. The skin is preferably "solvated" by the solvent, i.e. the intersticial and bound water is replaced thereby. Specified solvents are water-miscible alcohols and ketones, e.g. methanol, isopropanol, acetone, methyl ethyl ketone. Specified fatting agents are fatty acids (preferred) e.g. lauric, stearic, linoleic acids, natural oils of animal, vegetable and mineral origin, e.g. neat's-foot oil, cod-liver oil, caster oil, olive oil, mineral oils. Specifications 755,969 and 807,741 are referred to.

Waterproofing. Brit. Pat. 850,459. Du Pont de Nemours & Co., E. I. Filed Feb. 16, 1959.—Compounds of formula:



where X is



n is 2 or 3, no two X radicals are in adjacent positions on the benzene ring, and each of the R's is a C_1—C_{19} alkyl group, the sum of the carobn atoms in R_1, R_2, and R_3 being 10—21, are used for waterproofing permeable materials such as sole leather, textiles, and asbestos-cement siding used in the construction of dwelling-houses. Specified compounds of the above formula are N-substituted amides of terephthalic, isophthalic, and trimesic acids. The N-*t*-alkyl terephthalamides having alkyl groups in the C_{11} to C_{14} range are preferred. In an example, tanned leather is soaked in a solution of a C_{11}—C_{14} *t*-alkyl terephthalamide and after removal from the solution the leather is air-dried until free of solvent. The water-absorption of the leather is substantially reduced. In another example a cement-asbestos siding is rendered resistant to water-absorption by spraying it with an aerosol prepared from a solution comprising a *t*-alkyl trimesamide derived from a mixture of C_{11}—C_{20} *t*-alkyl amines, mineral spirits, and dichlorodifluoromethane.

Tanning Leather. Brit. Pat. 856,292. Commonwealth Engineering Co. of Ohio. Filed Sept. 30, 1958.—Aqueous alkaline solutions of water-soluble metal salts particularly tervalent chromium salts, such as chromium sulphate, which may be employed in tanning leather, having an hydroxyl ion concentration between 0.14N and 5.8N, which would normally precipitate an hydrous oxide, are stabilized, thereby preventing such precipitation, by adding a carboxymethyl ether of dextran or an alkali metal, e.g. sodium salt of the ether, said ether containing an average of from 1.0 to 3.0 carboxymethyl groups per anhydroglucose unit of the dextran, in an amount such that the equivalent ratio of the carboxymethyl ether of dextran anion to the metal cation is from 0.5 to 5.0. The

ether has a molecular weight between 2,000 and that of native, unhydrolysed, microbiologically produced dextran. Other metal salts include the salts of beryllium, aluminum, scandium, lanthanides, actinides and the transition and post-transition metals of the long periods.

Tanning Agents. Brit. Pat. 747,675. Farbenfabriken Bayer Akt.-Ges. Filed May 26, 1953.—Solid pulverulent tanning agents which readily dissolve in cold water to give clear solutions having the same properties as the initial syrupy products in that they are good tanning agents compatible with vegetable tannins and capable of dispersing and dissolving the sludge and phlobaphene of organic tanning solutions are obtained by evaporating an aqueous syrupy solution of a condensation product of an aldehyde, an *o*-chlorophenol and a mono- or di-sulphonic acid of a polynuclear hydrocarbon (*see* Group IV(a)), preferably after neutralizing, and adding to the resultant solid product solid acid reacting substances, e.g. sodium bi-sulphate, oxalic acid and citric acid. Specification 430,343 is referred to.

Oiling and Waterproofing Leather. Brit. Pat. 850,929. Stockhausen, J. Filed May 10, 1957.—Leathers may be oiled and waterproofed by means of an oiling agent obtained by oxidizing wool fat with air or oxygen and simultaneously or subsequently treating with an alkali metal bisulphite or pyrosulphite, under specified conditions (*see* Group IV (b)) to give a product capable of forming a colloidal solution in water. The wool fat may be oxidized in the presence of other oxidizable fats or fatty oils, e.g. train oil. Electrolyte-resisting emulsifying agents may be present during the oxidation or sulphite treatment or may be added to the product; agents suitable are oxyethylated fatty alcohols, sulphonated fatty acids, ethylene oxide-alkyl phenol condensates and C_{8-10} alkyl sulphonates. Conventional oiling agents may also be present. Mineral, chrome and vegetable tanned leathers and also furs and pelts may be treated. In examples: (1) an oiling-agent prepared as above from wool fat is used either in liquoring Persian lamb-skins or, with a polyglycol train oil acid ester, in oiling a vegetable tanned leather; (2) an oiling agent derived from a mixture of wool fat and cod-liver oil is used in oiling chrome-leather; (3) an oiling agent derived from a mixture of wool fat and sperm oil is mixed with an oleyl alcohol-ethylene oxide condensate and used to oil, and tan with Chromosal B, a chrome-tanned unhaired cow-hide.

Impregnating Leather. Brit. Pat. 857,120. Imperial Chemical Industries Ltd. Filed Aug. 31, 1959.—Leather is treated by first impregnating it with castor oil, or castor oil admixed with up to 50% of another oil and subsequently applying an organic compound containing two or more isocyanate groups, the quantity of the treating agents being such that the dry weight of the leather is increased by from 1—100%. Additional oils specified are cod oil, sperm oil, or degras. The oil may be applied by dipping, soaking, drumming, brushing, padding or spraying. The polyisocyanates may be 2:4-tolylene diisocyanate, hexamethylene diisocyanate, diisocyanato diphenylmethane, $4:4^{1}:4^{11}$-triisocyanate triphenyl-methane, and the reaction products of isocyanates with phenols and polyhydroxy compounds; and these compounds may be used as a solution in a solvent such as toluene, xylene or methyl ethyl ketone. Curing may be effected at

40° to 140°C. for periods up to 8 hours. The product is resistant to water and oil, and is suitable for soling shoes, for transmission belting, for oil seal washers and for clothing leather.

Waterproofing Fibrous Materials. Brit. Pat. 849,111. General Electric Co. Filed Nov. 19, 1956.—Fibrous sheet material, e.g. textiles, leather, paper, asbestos or sheet fibre material, are rendered water-repellent by immersion in a solution (e.g. toluene xylene or butanol) or an aqueous emulsion of a composition comprising, by weight, (1) from 25 to 75% of a liquid methylhydrogen siloxane, (2) from 75 to 25% of a polymerizable, liquid, non-resinous, intercondensed hydrolysate of a mixture, by weight, of 50 to 75% dimethyldichlorosilane, 1 to 10% trimethylchlorosilane, 10 to 35% methyltrichlorosilane and 0 to 10% of a methylchlorodisilane, and (3) a curing agent selected from stannous octoate, oleate and naphthenate, the curing agent being added in amount such that the stannous ion is equal to at least 1% of the total weight of (1) and (2) (*see* Group IV (a)), and thereafter heating the treated material, e.g. at 75° to 250° C. for ½ minute to ½ hour to cure the siloxane mixture. The compositions may also contain water-soluble urea- or melamine-formaldehyde resins and colloid protectors. Examples are given in which various textile materials are treated as above. Specification 575,667 is referred to.

Resin Dispersions; Finishing and Coating Leather. Brit. Pat. 850,390. Imperial Chemical Industries Ltd. Filed Feb. 10, 1958.—Leather is finished by treatment, e.g. by padding and/or spraying with a plasticized aqueous dispersion of a polymer or co-polymer of at least one acrylic or methacrylic ester, the plasticizer used containing a sulphonamide group and thereafter treating with formaldehyde. Stabilizers and emulsifiers e.g. long-chain sulphates or sulphonates, soaps, ethylene oxide condensates; colloidal stabilizers, e.g. casein, gums, starches, polyvinyl alcohol; other known adjuvants, e.g. pigments, dyestuff solutions, wax emulsions and minor amounts (less than 50% by weight) of other polymerizable ethylenically unsaturated monomers, e.g. vinyl esters, styrene, butadiene, acrylamide and methacrylamide may be included in the dispersion. Specified esters are the methyl, ethyl, propyl, butyl, β-ethoxyethyl and nonyl esters of acrylic and methacrylic acids. Specified plasticizers are the N-ethyltoluenesulphonamides.

Proofing Against Pests, Mould and Bacteria. Brit. Pat. 856,452. Farbenfabriken Bayer A. G. Filed June 9, 1958.—Textile materials, furs and skins are protected against the attack of textile pests, mould and bacteria by impregnation with an agent containing as active ingredient a haloalkyl-, haloaralkyl-, and/or haloaryl-sulphonamide of an aminodiphenylamine or N-iminosubstituted aminodiphenylamine, which is halogenated in one or both of the aromatic nuclei. The halogen may be fluorine, chlorine or bromine. The active ingredient may be applied in solution in an organic solvent, or as its water-soluble salt, e.g. the sodium salt, in aqueous solution. Many examples of active compounds are given in the Specification. Specification 738,758 is referred to.

Tanning Leather. Brit. Pat. 849,876. Toten Cellulosefabrik A.S. Filed March 19, 1959.—In a tanning process of the kind in which the hides are pre-treated with a cellulose extract, both the pre-tanning and the main tanning are effected continuously in a tanyard divided into a pre-tanning stage consisting of a number of vats through which a cellulose extract circulates, being led into the last of such vats and out of the first, the hides being moved in counter-current thereto, and a main stage consisting of at least some of the remaining vats wherein the main tanning is effected. Preferably, the pre-tanning is effected at a *p*H of 3.5—4.5, at 20—25° C., without the addition of salt, and using ammonium bisulphite lye. In the example, of a tanyard consisting of 7 vats each about 10 m.^{3} volume, 2 were used in the pre-tanning stage and the remainder for the main tanning; formic acid was used to adjust the *p*H of the ammonium bisulphite lye used in pre-tanning and the main tanning liquor was an extract consisting of 1/3 chestnut, 1/3 mimosa and 1/3 quebracho.

Coated Fabrics. Brit. Pat. 853,384. Imperial Chemical Industries Ltd. Filed Oct. 1, 1958.—Substrates are coated with polyurethanes by applying consecutively at least one polyester or polyesteramide and at least one polyisocyanate, the polyester or polyesteramide being applied in the form of an aqueous dispersion free from any soap or dispersing agent except alkali. The polyester or polyesteramide may be partially pre-reacted with a polyisocyanate. The aqueous dispersion may be applied by spreading, dipping or spraying. The polyisocyanate may be applied similarly as a solution or dispersion in an organic liquid. The substrate may finally be heated or may be left to cure at room temperature. Substrates which may be coated include natural and synthetic rubber, fabrics including polyethylene terephthalate and nylon, leather, paper and metals.

Waterproofing Leather. Brit. Pat. 850,726. Nopco Chemical Co. Filed May 26, 1959.—Leather is waterproofed with an aluminium salt of an aliphatic monocarboxylic acid having a carbon chain length of 12 to 24 carbon atoms by impregnating separately with an aromatic hydrocarbon solution of aluminum *iso*propoxide and an aromatic hydrocarbon solution of the acid, followed by washing in an aromatic hydrocarbon. Either the acid solution or the aluminium *iso*propoxide solution may be used first. Suitable acids are lauric, myristic, palmitic, stearic, behenic, oleic and ricinoleic acids, and mixtures thereof. Suitable solvents are benzene, toluene and xylene.

Impregnated Leather and Means of Producing. U. S. Pat. 2,983,566. S. S. Kreman and R. L. Southwood, Cincinnati, Ohio, assignors to Leather Research Corporation, New York, N. Y., a corporation of Delaware. Filed Apr. 18, 1958.—7. The method of producing impregnated hide substance which comprises impregnating porous hide substance with a solution of a water insoluble impregnant which is not a tanning agent for the hide substance, rinsing the wet hide substance with a solvent for the impregnant which contains no more than a small amount of said impregnant to reduce the concentration of impregnant in the outer layers of the hide substance, precipitating the impregnant in the hide substance by treatment with an extraction medium which is a solvent

for the impregnating solvent and a non-solvent for the impregnant, and then removing the extraction medium to leave the impregnant in the hide substance in greater concentration in the center than in the outer layers.

Extraction of Collagen. U. S. Pat. 2,979,438. J. H. Highberger, Marblehead, Mass., assignor to United Shoe Machinery Corporation, Flemington, N. J., a corporation of New Jersey. Filed Aug. 7, 1958.—1. A process for extracting collagen in soluble, reconstitutable form from skin material which comprises immersing the skin material in an aqueous solution containing the enzyme fraction salted out from a pH 4 to 5 aqueous extract of pancreas by ammonium sulfate by increasing the concentration of ammonium sulfate from an initial value of 20% of saturation to a final value of 40% of saturation, incubating the skin material in said solution at a pH in the range of 7 to 9 for at least ¼ of an hour at approximately 37° C. to break the linkages holding collagen against solution, removing said skin material from said solution before substantial degradation of the collagen and soaking the skin material in an aqueous extraction bath having a pH of 3 to 4.5 and an ionic strength below 0.5 to dissolve a high proportion of the collagen content of said skin material and to form a concentrated solution of acid soluble collagen.

Aldehyde Tanning of Leather. U. S. Pat. 2,983,567. S. S. Kremen and R. L. Southwood, Cincinnati, Ohio, assignors to Leather Research Corporation, New York, N. Y., a corporation of Delaware. Filed Apr. 18, 1958.—4. The method of tanning with formaldehyde which comprises treating hide substance with an impregnating solution consisting essentially of formaldehyde in an organic solvent containing insufficient water to cause tannage of the hide substance by the formaldehyde, treating the hide substance with an organic solvent for formaldehyde containing substantially less formaldehyde than in the impregnating solution to substantially reduce the formaldehyde content of the surface layers and then treating the hide substance with water to cause the formaldehyde to react with the hide substance, to produce a leather having substantially more formaldehyde combined with hide substance in the interior of the leather than in the outer layers thereof.

Purification of Collagen. U. S. Pat. 2,973,302. A. Bloch, Highland Park, and I. B. Oneson, Somerville, N. J., assignors to Ethicon, Inc., a corporation of New Jersey. Filed Feb. 5, 1958.—1. In a process for preparing a dispersion of swollen collagen fibers in a aqueous acid solvent, the improvement comprising: treating finely divided connective tissue which is substantially free from fat and muscle tissue with a solution of an elastase at a temperature within the range of from about 5° C. to about 45° C., the pH of the treating solution being within the range of from about 5 to about 9, whereby all elastin is removed without altering the collagen present in said connective tissue and removing the elastase adsorbed on the residual collagen fibers to avoid destruction of said collagen fibers.

Treatment of Wool with Acid Anhydrides in the Presence of Dimethylformamide. U. S. Pat. 2,986,445. N. H. Koenig, El Cerrito, Calif., assignor to the United States of America as represented by the Secretary of Agriculture. Filed Jan. 6, 1960.—1. A process for chemically modifying wool which comprises reacting wool under essentially anhydrous conditions, in the presence of dimethylformamide, with an acid anhydride of the class consisting of aliphatic, aromatic, and aromatic-aliphatic acid anhydrides, at a temperature about from 25° to 135° C. until the wool combines with about from 1 to 35% of its weight of the acid anhydride.

Waterproofing; Water-Repellent Coatings. Brit. Pat. 853,619. Rohm & Haas Co. Filed Jan. 31, 1957.—Leather, paper, wood, metal, glass and cotton, wool, rayon and other substrates are treated, to render them water-repellent or shrinkproof, with thermoplastic ethylenic addition polymers or copolymers of vinyl compounds of the general formula

$$CH_2 = CHXAOCH_2CH\text{——}CH_2$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad \backslash\ /$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\ O$$

or with amino-plast resin-forming condensates, such as urea or melamine-formaldehyde condensates, in which are incorporated a monomeric vinyl compound of the given formula, or a thermoplastic addition polymer thereof, X representing oxygen or sulphur and A denoting a C_2—C_{12} alkylene group which may or may not be substituted by a cycloalkyl, aryl or aralkyl group and which provides at least two carbon atoms between the O and X atoms or, alternatively, A denoting a group wherein X^1 represents oxygen or sulphur, n is an integer

$$-(C_nH_{2n}X^1)_xC_nH_{2n}-$$

from 2–12 and x an integer from 1 to 5 there being at least two carbon atoms between each adjacent pair of hetero atoms in the group —XAO—. The treated materials may be cured or baked, suitably in the presence of an acid catalyst to effect a cross-linking via the epoxy groups.

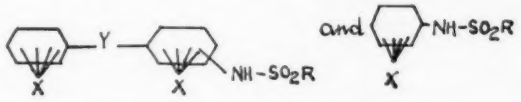
Artificial Leather. Brit. Pat. 748,046. Deutsche Gold- und Silber-Scheideanstalt Vorm. Roessler. Filed Oct. 23, 1953.—Artificial leather is manufactured by coating a substrate, e.g. cotton twill, with a composition polyvinyl chloride, a plasticizer, a pigment, at least 3 per cent of a swellable macromolecular substance which does not dissolve in or react with polyvinyl chloride, and a swelling agent for the macromolecular substance which is either water or an organic liquid which has no solvent action on polyvinyl chloride and volatilizes at the temperature at which the polyvinyl chloride is gelled, said swellable macromolecular substance being present in the composition as discrete particles and said swelling agent being present in the composition in an amount which swells the macromolecular substance but is insufficient to form a dispersion or macromolecular solution therewith, and heating to get the polyvinyl chloride. Macromolecular substances swellable in water include starch, dextrin, pectin,

alginates, casein, gelatin, methyl cellulose, cellulose glycollate salts, agar-agar, polyamides, polyvinyl alcohol, polyacrylic and polymethacrylic acid salts. Organic swelling agents specified are methanol, ethanol and benzine. Macromolecular substances swellable in organic solvents are polyvinyl acetate and acetal, polyamides, benzyl cellulose and polystyrene. Up to 10 per cent, preferably 0.2–5 per cent, of blowing agents may be included, e.g. ammonium carbonate and bicarbonate, percarbamide, iron oxalate, ethyl malonic acid, citric acid, azodibutyric acid nitrile, *o*- and *m*-benzoic acid, *n*-azoxy-benzoic acid, benzoyl peroxide, hydrazobenzene, and diaminodiphenylamine. A hydrophilic filler may also be included, e.g. flocks of cotton, staple fibre, artificial silk, paper, wood, cork, or leather meal, leather powder, animal hair, bentonite, silica gel. Conventional plasticizers, e.g. dioctyl phthalate, may be partly or completely replaced by acetylated castor oil.

Waterproofing Paper, Leather and Textiles. Brit. Pat. 748,016. Ciba Ltd. Filed Aug 28, 1952.—Water resistance is imparted to paper, leather or textiles by treatment with aqueous solutions of water-soluble salts, which may be quaternary ammonium salts, obtained by reacting together methylol compounds of amino-triazines or urea or their ethers with low molecular alcohols, non-basic aliphatic compounds which contain a carbon chain of at least 7 carbon atoms and a reactive hydrogen atom attached to an oxygen atom, a sulphur atom or a non-basic nitrogen atom, and primary or secondary amines which contain in the molecule a reactive hydrogen atom attached to another hetero atom, the resultant bases finally being converted into water-soluble salts if necessary (*see* Group IV (a)), followed by heating at an elevated temperature with or without intermediate drying. To the treating baths may be added aluminum and zirconium salts and other salts of weak acids, sols of hydrated zirconium dioxide, paraffin wax dispersions, solvents, methylolamides, protective colloids, finishing or matting agents such as methylol ureas, and wetting or softening agents. In example 19, cotton gabardine is impregnated with an aqueous composition which contains ammonium chloride, formic acid and an emulsion of paraffin wax and the acetic acid salt of the reaction product of triethanolamine with the product obtained by reacting methylated methylol melamine and stearic acid. The fabric is dried and after-treated for five minutes at 120° to 150° C. Example 20 is similar but omits paraffin wax. Similar results are obtained using (a) the acetic acid salt of the reaction product of triethanolamine and the products obtained by reacting a highly methylated methylol melamine partly with stearic acid and partly with N-methylol stearic acid amide; (b) the acetic acid salt of the reaction product of triethanolamine with the product obtained by reacting methylated methylol melamine and N-methylol octadecylurethane; (c) the acetic acid salt of the reaction product of methlyol melamine methyl ether with the condensation product from 2 mols. stearic acid and 1 mol. diethylene triamine; (d) the acetic acid salt of the reaction product of dimethylol urea dimethyl ether and the condensation product from 2 mols. stearic acid and 1 mol. of diethylene triamine. Specifications 611,012, [*Group* IV (a)], and 662,548 are referred to.

Proofing Wool, Hides and Furs Against Biological Attack. Brit. Pat. 854,956. Farbenfabriken Bayer A.G. Filed Nov. 25, 1957.—Wool, hides and

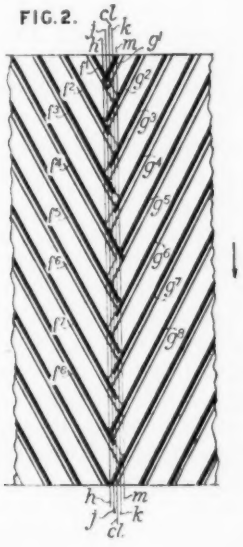
furs are protected against pests, fungi and bacteria by compounds containing the trifluormethyl radical —CF_3 and having the general formulæ



wherein X stands for hydrogen, chlorine or CF_3, at least one X being CF_3, R stands for a chloroalkyl-, chlorocycloalkyl-, chloroaryl- or chloroaralkyl radical, and Y stands for O, S, SO, SO_2, CH_2, or a diphenyl linkage. For the preparation of these compounds *see* group IV (b). In Example (7), products of wool or unions are treated, similarly to dry-cleaning, in organic solvents containing 0.1 to 1% of 2-chloromethane - sulphonylamino - $2^1,4^1$ - dichloro - 4 - trifluoromethyl - diphenylether. In Example (8), wool or unions are treated in an aqueous solution of 1 gram per litre of an alkali metal salt of 2 - chloromethane - sulphonylamino - $2^1,4^1$ - dichloro - 4 - trifluoromethyl - diphenylether at 20—60° C. for ½ to 1 hour and dried after draining. In Example (11), wool is protected by treatment with a solution of 2 - chloro - 5 - trifluoromethyl - chloromethane-sulphonyl-aminobenzene. In Example (12), wool is protected by treatment in a dilute aqueous solution of the sodium salt of 2-chloro - 5 - trifluoromethyl - 1 - chloromethane - sulphonyl - aminobenzene. Specifications 702,602, 709,455 and 738,758 are referred to.

Leather Shaving Apparatus; Setting Out Leather. Brit. Pat. 853,777. Wilson & Son Ltd., E. Filed April 30, 1959.—A shaving or setting out roller

FIG. 2.



for use in the treatment of leather, comprising two series—one right hand and the other left hand—of helically curved blades set in right-hand and left-hand helical grooves of the roller is characterized in that the adjacent ends of the operative cutting edges of complementary pairs of right- and left-hand blades terminate without overlap, so far as is practicable, at points which are uniformly spaced, in an axial direction of the roller, within an area extending on each side of the peripheral transverse centre line of the roller. As shown, blades f^1, f^2, f^3, f^6, f^7 and f^8 together with complementary blades g^1, g^2, g^3, g^6, g^7 and g^8 are arranged with their operative cutting edges terminating on lines *h*—*h*, *j*—*j*, *cl*—*cl*, *k*—*k*, *cl*—*cl* and *j*—*j* respectively, line *cl*—*cl* denoting the transverse centre line of the roller. Blades f^4 and g^5 abut one another and blades g^4 and f^5 terminate on line *k*—*k*. With the blades so arranged, the portion of the roller's periphery which contains the inner ends of the two series of blades, i.e. the area bounded by lines *h*—*h* and *m*—*m* has substantially the same cutting or shaving potential as the remainder of the roller.

BOOK REVIEW

Fellmongers Handbook. M. S. Carrie and F. W. Woodroffe. New Zealand Leather and Shoe Research Association (Inc.), Information Series No. 25, New Zealand Department of Scientific and Industrial Research, 1960. 108 pp. Price 12s. 6d. R. E. Owen, Government Printer, Wellington, New Zealand.—This excellent little practical manual is one of a series published by the New Zealand Department of Scientific and Industrial Research. The authors are two well known New Zealand authorities on the "fellmongering" process, called "wool pulling" in the United States. Mr. M. S. Carrie is chief chemist of the Canterbury Frozen Meat Company, Ltd., and Mr. F. W. Woodroffe is the Director of Research of the New Zealand Leather and Shoe Research Association in Wellington. This book is written for the practical man in the factory who has the responsibility for the day-to-day production of pickled lambskins and sheepskins. The book sets forth in elementary chemical language the basis of the various processes and materials used, together with a number of micro-photographs illustrating the structure of good and unsatisfactory skins. In the reviewer's opinion, there is a need—certainly in the U. S. A.—for similar small manuals or books describing the processing of different types of hides and skins through the beamhouse, tanning department, and finishing department. Such books would form a welcome bridge between the more lofty publications of the research associations and the simple descriptions in trade journals and in

pamph'ets of supply houses. This book, of course, deals exclusively with New Zealand practice, which is quite different from American practice for the production of pulled wool and pickled sheepskins. In New Zealand today, apart from the depilatory painting using lime and sulfide, the skins are universally processed in "dollies", corresponding to "paddles" in the U. S. A. Some of the statements in regard to operation, amounts, chemicals, and so on, must be transcribed to our basis for them to be meaningful. The point of this is that in the U. S. A. and in South America with the large meat packers and the larger independent operators the "drum" process is widely used, yet there is no mention at all of it. There are a number of statements surprising to us in the light of our differing experience. Among them we find the following: *p. 30*—It is said that calcium carbonate is commercially referred to as "lime". This is not the case in the United States where calcium carbonate is called limestone or agricultural limestone. "Lime", which is also used by the farmer, is hydrated lime, i.e., calcium hydroxide. *p. 41*—The statement that acetic acid is a satisfactory depilatory is an erroneous one. The method has been examined here and found to be deficient. Certainly in no way does it compare with the ease of wool removal obtained by using sulfide depilatories, and it is a fact—as far as the reviewer knows—that acetic acid is not used anywhere today, and certainly not in the United States. *p. 44*—In the chapter on depilation and liming, it might be pointed out that in the United States a solution of simple sodium sulfide containing nothing else has been and is used quite successfully as a depilatory paint. *p. 49* In speaking of temperature and its influence on the depilating paint, one American technical innovation is to conduct the painting and the hanging of the skins in a cold chamber maintained at 60°F. *p. 56*—In discussing adjusting the sulfide in the liming process in the dollies, it seems to the writer that this leaves far too much to the judgment of operators, with, consequently, unnecessary variations in the quality of the skins. This matter, of course, is taken care of very well in the drum process in which the conditions can be kept under better control because no old liquors are ever used. *p. 69*—In the chapter on pickling, the contentious question of the amount of residual acid in the pickled skin is handled discreetly. It is surprising to the reviewer to know that too much salt produces a poor microstructure. We feel that, provided the salt does not spew out on the semi-dried skins, it is safer to have an excess of salt. We do not feel that this is in any way deleterious to the quality of the skins. *p. 79* (*Pieing*)— We must give considerable credit to the New Zealand invention of the Slipemaster machine and method of removing wool from skin pieces. The fact that this method has replaced the disgusting, old, putrefaction method is a credit to the New Zealand research scientists. *p. 82*—Interpretation of microphotographs shows the influence of the British school, namely, the British Leather Manufacturers' Research Association. However, we would caution the practical man to be very careful in drawing conclusions—certainly about the quality of skins—from photomicrographs. There have been cases in the past where good and

bad leather—bad even to the point almost of disintegration—have been indistinguishable under the microscope. However, the microscope is a very valuable tool, particularly for showing the presence of hair roots, fat cells, grain damage, and so on. In the opinion of the reviewer, this is a more important application of the microscope than trying to assess leather quality. *p. 94*—In the section on the faults, it is surprising that the term "mottle" is not discussed. This has been one of the chief criticisms about the New Zealand skins by the American buyers. This little book could be useful to many of our own "practical" men in the wool pulleries and even in the tanneries—not necessarily from the point of view of obtaining fresh information but on account of the simple picture that is presented of the whys and wherefores of using sulfide and lime, delimers, enzyme bates, and the pickling process. H. G. Turley

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The pace of technological change is accelerating. We cannot possibly foresee the progress or discoveries of tomorrow. We ought, therefore, to concentrate our efforts in imparting to prospective engineers a thoroughly fundamental technical competence, together with intellectual and moral self-reliance.

This means a greater emphasis on basic science—and every conference on engineering education in recent years has concurred in the need for a higher level of achievement in mathematics, physics, and chemistry. Yet while it is quite clear that the bonds between engineering and science are growing tighter, we could make no more disastrous error than to attempt to recreate the engineer in the image of a scientist. The engineer is concerned with means as well as with use and purpose, with ideas of design, cost, and reliability that are largely alien to the scientist. So much has been made recently of the need for more mathematics and physics that we are in danger of losing sight of the problem that remains in fact the most difficult in engineering education: how to balance theory with experiment, how to couple purpose and action with theoretical competence, and how to develop an appreciation of the empirical judgments that so often determine design.

—Julius A. Stratton, *The President's Report* **1960**. Massachusetts Institute of Technology.

With some qualifications, I believe that Russians have judged the situation sensibly. They have a deeper insight into the scientific revolution than we have, or than the Americans have. The gap between the cultures doesn't seem to be anything like so wide as with us. If one reads contemporary Soviet novels, for example, one finds that their novelists can assume in their audience—as we cannot—at least a rudimentary acquaintance with what industry is all about. Pure science doesn't often come in, and they don't appear much happier with it than literary intellectuals are here. But engineering does come in. An engineer in a Soviet novel is as acceptable, so it seems, as a psychiatrist in an American one. They are as ready to cope in art with the process of production as Balzac was with the processes of craft manufacture. I don't want to overstress this, but it may be significant. It may also be significant that, in these novels, one is constantly coming up against a passionate belief in education. The people in them believe in education exactly as my grandfather did, and for the same mixture of idealistic and bread-and-butter reasons.

—C. P. Snow. *The Two Cultures and The Scientific Revolution*. Cambridge University Press, 1959.

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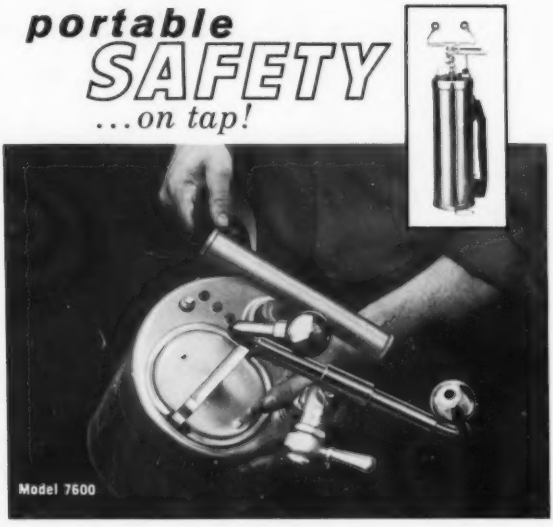

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